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CLAYS

WORKS OF PROFESSOR H. RIES

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CLAYS

THEIR OCCURRENCE, PROPERTIES, AND USES

WITH ESPECIAL REFERENCE TO THOSE OF
THE UNITED STATES AND CANADA

BY

HEINRICH RIES, PH.D.
Professor of Geology in Cornell University

THIRD EDITION, REVISED AND ENLARGED

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PREFACE TO THIRD EDITION

It is now some years since the second edition of this work appeared, and in endeavoring to revise it for a third edition the author has found the task no easy one because of the enormous amount of material which has appeared in the interval; and while every effort has been made not to overlook any important contributions, it is possible that some may have been missed, because of the great mass of literature that had to be gone through.

The general arrangement of the book remains the same, except that the sections on mining clays and manufacture have been omitted, and, in the areal treatment of clays, Canada has been added. So too has a section on Bentonite.

The author takes great pleasure in here acknowledging aid received from the Heckscher Research Fund Committee of Cornell University, as a result of which he was able to obtain assistance in the matter of searching through the literature.

Thanks are also due to the American Ceramic Society for permission to reproduce a number of illustrations from the Transactions and Journal, and to numerous State Geologists to whom acknowledgments are made in the text.

H. Ries

Cornell University, Ithaca, N. Y.
March, 1927.

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CLAYS

THEIR OCCURRENCE, PROPERTIES, AND USES

CHAPTER I

ORIGIN AND OCCURRENCE OF CLAY

Definition.—Clay is the term applied to those earthy materials occurring in nature whose most prominent property is that of plasticity when wet, on which account they can be molded into almost any desired shape. This shape is retained when dry, and the clay becomes hard and rocklike when heated to redness or higher. Mineralogically clay is made up of a variety of mineral fragments, ranging from fresh to decomposed ones, and in size from sand grains to particles under 1 μ in diameter. The very fine particles, which may be of colloidal character, cannot always be definitely identified.

From the standpoint of physical chemistry clays may be regarded as disperse systems of mineral fragments in which particles under 2 μ predominate.[1]

The colloidal matter may be of organic or inorganic character.[2]

Clays may be derived from fresh rocks either by the ordinary processes of surface weathering, or by the action of solutions which may be of igneous origin or indirectly of surface origin.

In either case the alteration product is residual in its character and the material might be called a *residual clay.*

These residual clays if exposed at the surface may then be removed by a transporting agent, such as water, and serve to form the great group of transported clays to be mentioned later.

---

[1] Oden, S., General introduction to the Chemistry and Physical chemistry of Clays, Geol. Inst. Univ. Upsala, Bull. XV, p. 175-194, 1916; also Trans. Faraday Soc., XVII, p. 327, 1922.

[2] Cushman, A. S., Jour. Amer. Chem. Soc., XXV, p. 5.

RESIDUAL CLAYS

Residual Clays Formed by Surface Weathering

The formation of clay by weathering processes may take place in several different ways, viz.:[1] (1) By decomposition of silicate minerals of the rock, the product having all the properties of clay; (2) by solution of a carbonate rock containing insoluble clayey impurities, which are left behind as an insoluble residue; (3) by the disintegration, accompanied possibly by some solution, of shales.

Clay Formation by Silicate Decomposition

The weathering of granite in the presence of moisture may serve as an example of this type.

In such a rock disintegration or mechanical breaking down of the rock opens up a pathway for the surface waters, which attack the silicates.

It has usually been supposed that the decomposition of the silicates in the rock, such as feldspar, is caused chiefly by the dissolved carbon dioxide, which is probably always present in the percolating waters, and this view was advanced by Forschammer as early as 1835,[2] as well as by other writers later;[3] but, as pointed out by Cameron and Bell,[4] this is very doubtful, in view of the fact that many of the minerals found in rocks are known to be soluble in water alone, although their solution may take place but slowly. The water, moreover, is believed to react with or hydrolyze them, as is shown by the fact that an alkaline reaction can be obtained with phenolphthalein, after treating powdered minerals with water free from dissolved carbon dioxide.

---

[1] For a general and detailed discussion of the subject, see especially: Merrill, G. P., Rocks, Rock-weathering and Soils, 1897; Buckman, H. O., Trans. Amer. Ceram. Soc., XIII, p. 336, 1911.

[2] Pogg. Ann., XXXV, p. 331, 1835.

[3] Rogers, Amer. Jour. Sci., V, p. 404, 1848; Bischof, Naturhist. Ver. Bonn, XII, p. 308, 1855; Daubrée, Compt. ren., LXIV, p. 339, 1867; Miller, Tscherm. Mitth., 1877, p. 31; Butler, Min. Mag., XVI, p. 63; Parsons, Amer. Min., VIII, p. 157, 1923.

[4] Bur. of Soils, Bull. 30, p. 16, 1905; also Cushman and Hubbard, Bull. 28, Office of Public Roads, Washington.

In certain cases the view has been advanced that the CO_2 which took part in the weathering process was supplied by the leaching by surface waters of beds of peat or coal overlying the feldspathic rock.[1]

The rate of solubility varies, of course, with the different minerals, the magnesium-bearing micas being more soluble than muscovite, and albite more so than orthoclase, with oligoclase between.[2] Clark [3] found that muscovite, lepidolite, phlogopite, orthoclase, oligoclase, albite, leucite, nephelite, cancrinite, spodumene, scapolite, and many zeolites, all dissolve in water, giving an alkaline reaction, and the same has been shown of others.[4]

The action of water on orthoclase is assumed to be somewhat according to the following formula: [5]

$$KAlSi_3O_8 + HOH = KOH + HAlSi_3O_8.$$

The potassium hydrate thus formed may unite with carbon dioxide to form either a carbonate or bicarbonate of potash, or it is possible that it may unite with other acids, forming salts more soluble than the orthoclase in the hydrolyzed acid.

The $HAlSi_3O_8$ formed is apparently unstable, and may lose some of its silica, resulting in the formation of kaolinite, pyrophyllite, or diaspore, but the first of these appears to be more commonly formed in the weathering of feldspar.

The reaction more commonly given for the decomposition of orthoclase is

$$K_2O \cdot Al_2O_3 \cdot 6SiO_2 + 2H_2O + CO_2 = Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O + K_2CO_3 + 4SiO_2.$$

Kaolinization.—This alteration of the feldspar is termed *kaolinization.* The changes which take place in the alteration of several species of feldspar may be given as follows:

---

[1] Rohland, Sprechsaal, XLV, p. 51, 1912; Niggli, P., Lehrbuch der Mineralogie, p. 594; Endell, K., Sprechsaal, XLIII, p. 278 and 291, 1910.

[2] Merrill, Rocks, Rock-weathering and Soils, p. 234, 1897.

[3] U. S. Geol. Surv., Bull., 167, p. 156, 1900.

[4] See Bull. 30, Bur. of Soils, for numerous references on this subject; also H. Stremme, Zeitschr. prak. Geol., XVI, p. 122; also Clarke, U. S. Geol. Surv., Bull. 770, p. 481–486, 1924; Steiger, G., U. S. Geol. Surv. Bull. 167, 1900.

[5] Cameron and Bell, l. c., p. 18.

	SiO_2	Al_2O_3	K_2O	H_2O	Per cent
Orthoclase	64.86	18.29	16.85	....	100.00
Lost	43.24	....	16.85	....	60.09
Taken up	....	....	....	6.45	6.45
Kaolinite	21.62	18.29	....	6.45	46.36
			Na_2O		
Albite	68.81	19.40	11.79	....	100.00
Lost	45.87	....	11.79	....	57.66
Taken up	....	....	....	6.85	6.85
Kaolinite	22.94	19.40	....	6.85	49.10
			CaO		
Anorthite	43.30	36.63	20.07	....	100.00
Lost	....	....	20.07	....	20.07
Taken up	....	....	....	12.92	12.92
Kaolinite	43.30	36.63	....	12.92	92.85

It will be seen from this that both the orthoclase and plagioclase might yield kaolinite; in fact the plagioclase varieties decompose more readily than orthoclase.[1]

Vogt [2] has recorded an occurrence of kaolin near Jösingfjord, at Ekersund-Soggendal, Norway, which is formed from labradorite, the different states in the change being indicated by the following analyses:

	Labradorite	Labradorite partly kaolinized		Massive kaolin, more or less pure					Kaolinite
		I	II	I	II	III	IV	V	
Silica (SiO_2)	54.5	50.03	49.16	48.61	48.06	47.83	47.72	46.85	46.50
Alumina (Al_2O_3)	27.0	28.60	29.60	29.45	38.57	34.53	37.40	37.56	39.56
Iron oxide (Fe_2O_3)	2.5	1.62	1.88	3.40		1.70	1.59	1.00	
Lime (CaO)	9.0	4.21	3.47	.68	Undet.	.48	.23	Tr.	
Magnesia (MgO)	1.0	2.95	1.67	.49		.59	.11	Tr.	
Potash (K_2O)	1.0	1.00	Undet.	Undet.		Undet.	.44	Undet.	
Soda (Na_2O)	5.0						.76		
Water (H_2O)	......	11.90	13.63	16.38	12.95	13.76	11.66	14.44	13.94
Total	100.0	100.31	(99.41)	(99.01)	(99.58)	(98.89)	99.91	(99.85)	100.00

---

[1] Ries, Kaolins and fire-clays of Europe, U. S. Geol. Surv., 19th Ann. Rept. pt. VI (ctd.), p. 337, 1898; Leimberg, Zeitsch, d. d. Geol. Ges., Vol. 35, 1883; Rösler, Neues Jahr., Beil. Bd. XV, 2d Heft, p. 231.

[2] Amer. Inst. Min. Eng., Trans., XXXI, p. 151, 1902.

Prof. Vogt believes that the kaolinization here is due to the action of carbonic-acid waters, because calcite occasionally occurs with the kaolin. However, from what has been said on page 3, the presence of this mineral would not necessarily show that the acid above mentioned had assisted in the decomposition of the feldspar, but simply that it had united with the lime set free during the breaking up of the labradorite.

While it is probable that other silicates, such as hornblende or augite, yield a hydrous aluminum silicate, it is not known that it is kaolinite,[1] but their decomposition no doubt proceeds in a manner similar to that of feldspar.

Vogt,[2] on the other hand, states that hornblende, augite, beryl, topaz, etc., are known to be occasionally converted into kaolinite, but gives no evidence.

Quartz, although apparently resistant, is not left untouched, for it too is slightly soluble, but, aside from that originally present in the rock, silica may have been liberated during the decomposition of some of the silicates, such as feldspar.

It has been found that in soils, and the same may be said of clays, quartz has accumulated in relatively large proportions. It may be present as quartz, colloidal silica, or perhaps other forms. There is, however, a tendency for it to be gradually changed over into other forms of quartz through solution and redeposition.[3]

While there is undoubtedly lack of absolute proof that silicates other than feldspar yield kaolinite, all clays appear to contain a variable amount of some hydrated silicate of alumina, which may be present in some quantity, since it is a highly insoluble natural compound; and even though the statement is frequently made that this silicate is the mineral kaolinite, the fact is at times somewhat difficult of proof; indeed the evidence is clearly against it in some cases.

This hydrated aluminum silicate was formerly sometimes referred to as the clay substance or clay base, on the supposition that kaolinite was the basis of all clays. It has been recognized for some years however that this view is incorrect, and that a clay may have very little kaolinite. In spite of this, the old idea regarding the mineral composition of clay is still quoted in the literature.

Hickling [4] has suggested that muscovite may be an intermediate compound in the alteration of feldspar to kaolinite, and Galpin[1] has corroborated this view.

---

[1] Merrill, Rocks, Rock-weathering and Soils, p. 21, 1897.

[2] Problems in the Geology of Ore Deposits, Trans. Amer. Inst. Min. Eng., XXXI, p. 151, 1902.

[3] Hayes, Bull. Geol. Soc. Amer., VIII, p. 213, 1897, and Jour. Geol., V, p. 319, 1897.

[4] Hickling, G., China clay; its nature and origin. Inst. Min. Eng. (England), Trans., XXXVI, p. 10, 1908–9.

The presence of feldspar is not necessary to yield residual clay from a silicate rock by weathering. There are some rocks which contain no feldspar (such as serpentine), and some basic igneous rocks with very little, which on weathering produce some of the most plastic clays known.

ORIGIN BY SOLUTION

Many limestones, dolomites and gypsum contain clayey impurities. Penetration of the rock by surface water will cause solution of the carbonates or sulphate leaving the more or less insoluble clay behind. This is further referred to under Residual clay.

ORIGIN BY DISINTEGRATION

Shales are but consolidated clays, the consolidation in many cases being solely the result of pressure, in other cases both pressure and cementation being involved. Disintegration by frost and infiltrating water may therefore in many instances cause the shale to slake down to soft clay once more. If the shale is calcareous (or gypsiferous), solution may also be operative.

Removal of iron.—While as a rule there seems to be a relatively small loss of iron in the process of weathering, it is probable that under favorable conditions, an appreciable quantity may be extracted. This is supposed by some to be the case if a rock which is undergoing weathering to residual clay is overlain by a deposit of organic material like peat which might yield carbonic and organic acids to the percolating waters.[2] Instances of this are probably not common but they do occur.

Relation of residual clay to underlying bed rock.—Many different kinds of rock yield residual clay by weathering, but the nature of the material is more or less influenced by the character of the parent rock.

Decomposition of the rock begins at the surface and extends downward to the depth reached by the weathering agents.

In the case of rocks made up largely or wholly of silicates like igneous rocks, schists, gneisses, and feldspathic quartzites there is usually a gradual transition from the fully decomposed rock (clay) at the surface into the parent rock beneath, an intermediate zone being made up of rock fragments surrounded by clay (Fig. 1).

---

[1] Galpin, S. L., Studies of Flint Clays and their associates. Amer. Ceram. Soc., Trans., XIV, p. 301, 1912.

[2] For a summary of opinions in favor of this theory see Howe, J. A., Handbook of Kaolin, China Clay and China Stone, Mus. Prac. Geology, London, 1914.

A similar condition exists in residual clay from shales.

A marked exception to the above is seen in the case of residual clay derived from limestone, where the passage from clay to rock is sudden. The reason for this is that the change from limestone into clay does not take place in the same manner as granite. Limestone consists of carbonate of lime, or carbonate of lime and magnesia, with a variable quantity of clay impurities, so that when the weathering agents attack the rock, the carbonates are dissolved out by the surface-waters, and the insoluble clay impurities are left behind as a mantle on the undissolved rock, the change from rock to clay being, therefore, a sudden one, and not due to a gradual breaking down of the minerals in the rock, as in the case of granite.[1]

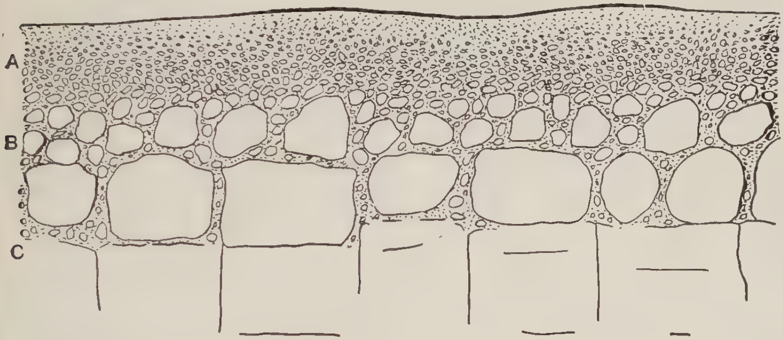

Fig. 1.—Section showing the passage of the fully formed residual clay on the surface into the solid bed-rock below. A, clay; B, clay and partly decomposed rock; C, bed-rock below, passing upwards into rock fragments with a little clay.

Kaolin.[2]—A residual clay derived from a rock composed entirely of feldspar, or one containing little or no iron oxide, is usually white and therefore termed a *kaolin;* deposits of this type may contain a high percentage of the mineral *kaolinite*,[3] this being assumed because, after washing the sand out of such materials, the silica, alumina, and water in the remaining portion are in much the same ratios as in kaolinite, although, as previously mentioned, other hydrous aluminous silicates may at times be present.

---

[1] For residuals from crystalline rocks see under Maryland, Virginia and Pennsylvania; for limestone and shale residuals under Virginia and Kentucky.

[2] Ries, Trans. Amer. Ceram. Soc., XIII, p. 51, 1911.

[3] The terms *kaolinite*, referring to the mineral, and *kaolin*, referring to the rock mass, are often carelessly confused even by scientific writers, although there seems to be little excuse for so doing.

A clay made up entirely of kaolinite or some related hydrous aluminum silicate is sometimes termed a "pure" clay, but since the term clay refers to a physical condition and not a definite chemical composition, it would perhaps be more correct to term kaolin the simplest form of clay.

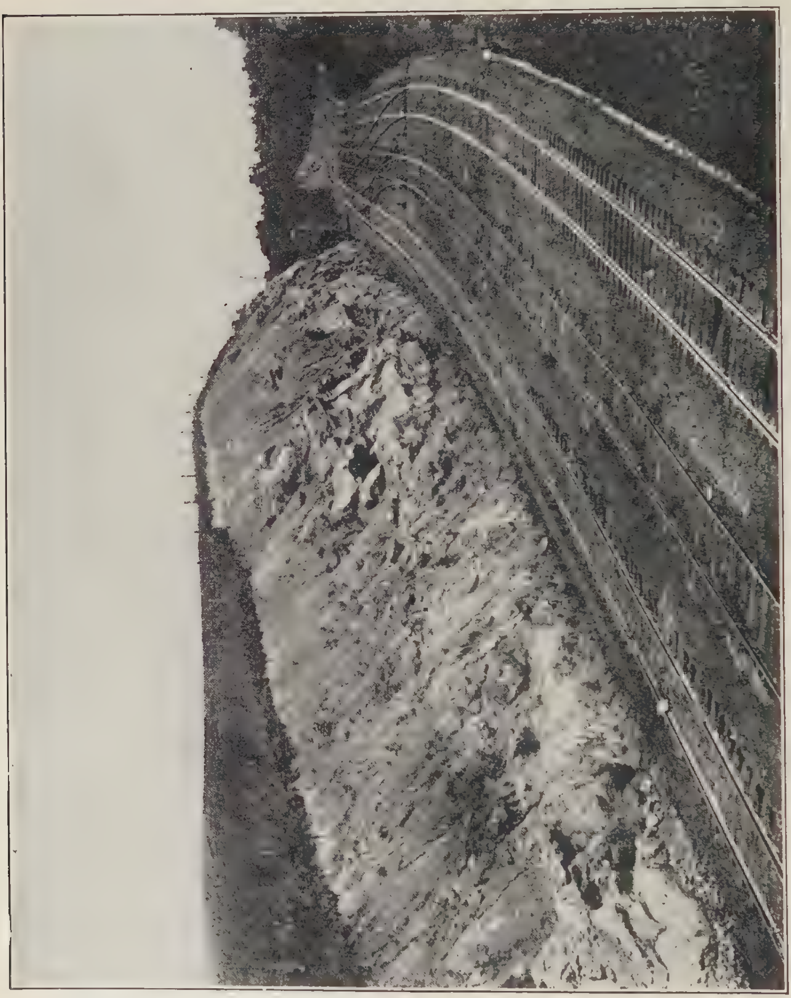

Fig. 2.—Residual clay from limestone at Christiansburg, Va.; shows uneven surface of parent limestone. (H. Ries, photo.)

There are clays made up almost entirely of other hydrous aluminum silicates than kaolinite, which are also termed kaolins, as the indianaite of Indiana, or the halloysite of Alabama.

A deposit of pure kaolinite has not thus far been found in nature though some very nearly pure occurrences are known. While the term kaolin is sometimes applied to any residual clay, the writer believes that this designation should be restricted to white residual clays, a usage which is wide-spread but has not become universal. The name *kaolin* is a corruption of the Chinese *Kauling*, which means *high ridge*, and is the name of a hill near Jauchau Fu, where the mineral is obtained.[1]

In this connection it is interesting to note that, according to Richthofen,[2] the rock from which the King-te-chin porcelain is made is not true kaolin, but a hard jade-like greenish rock which occurs between beds of slate. He states: "This rock is reduced, by stamping, to a white powder, of which the finest portion is ingeniously and repeatedly separated. This is then molded into small bricks. The Chinese distinguish chiefly two kinds of this material. Either of them is sold in King-te-chin in the shape of bricks, and as either is a white earth, they offer no visible differences. They are made at different places, in the manner described, by pounding hard rock, but the aspect of the rock is nearly alike in both cases. For one of these two kinds of material the place Kaoling ('high ridge') was in ancient times in high repute, and, though it has lost its prestige since centuries, the Chinese still designate by the name 'Kaoling' the kind of earth which was formerly derived from there, but is now prepared in other places. The application of the name by Berzelius to porcelain *earth* was made on the erroneous supposition that the white earth which he received from a member of one of the embassies (I think Lord Amherst) occurred naturally in this state. The second kind of material bears the name Pe-tun-tse ('white clay')."

The analyses[3] on p. 10 show the average composition of (I) the natural material from King-te-chin, such as is used in the manufacture of the finest porcelain; (II) that from the same locality used in the so-called blue Canton ware; (III) that of the English Cornwall stone; (IV) washed kaolin from St. Yrieux, France; and (V) washed kaolin from Hockessin, Del.

These analyses show a most striking difference between the two washed kaolins and the Chinese clay and Cornwall stone.

Kaolins are now known to have been formed by weathering from a variety of rocks as pegmatites (N. C.), limestone (Pa.), schist (Pa.), shale (Va.), feldspathic quartzite (Conn.),[1] granite (Cornwall, Eng.), syenite (Ark.), porphyry (Halle, Ger.) etc.

---

[1] Dana, System of Min., 1892, p. 687.

[2] Amer. Jour. Sci., 1871, p. 180.

[3] G. P. Merrill, Non-metallic Minerals, p. 224, 1904.

	I	II	III	IV	V
Silica (SiO_2)	73.55	73.55	73.57	48.68	48.73
Alumina (Al_2O_3)	21.09	18.98	16.47	36.92	37.02
Ferric oxide (Fe_2O_3)	....	....	.27	....	.79
Lime (CaO)	2.55	1.58	1.17	....	.16
Magnesia (MgO)	.15	1.08	.21	.52	.11
Potash (K_2O)	....	.46	5.84	.58	.41
Soda (Na_2O)	....	2.09			.04
Water (H_2O)	2.62	1.96	2.45	13.13	12.83
Total	99.62	99.70	99.98	99.83	100.00

Form of residual deposits due to weathering.—The form of such a residual clay deposit, which is also variable, depends on the shape of the parent rock. Where the residual clay has been derived from a great mass of granite or other clay-yielding rock, the deposit may form a mantle underlying a considerable area. On the other hand, some rocks, such as pegmatites, occur in masses having but small width as compared with their length, and in this case the outcrop of residual clay along the surface will form a narrow belt.

Clay derived from a rock containing much iron oxide will be yellow, red, or brown, depending on the iron compounds present. Between the white clays and the brilliantly colored ones others are found representing all intermediate stages, so that residual clays vary widely in their color.

The depth of a deposit of residual clay will depend on climatic conditions, character of the parent rock, topography, and location. Rock decay proceeds very slowly, and in the case of most rocks the rate of decay is not to be measured in months or years, but rather in centuries. Only a few rocks, such as some shales or other soft rocks, change to clay in an easily measurable time. With other things equal, rock decay proceeds more rapidly in a moist climate, and consequently it is in such regions that the greatest thickness of residual materials is to be looked for. The thickness might also be affected by the character of the parent rock, whether composed of easily weathering minerals or not. Where the slope is gentle or the surface flat, much of the residual clay will remain after being formed, but on steep slopes it will soon wash away.

---

[1] U. S. Geol. Surv., Bull. 708, p. 17 et seq., 1922.

In some cases the residual materials are washed but a short distance and accumulate on a flat or very gentle slope at the foot of the steeper one, forming a deposit not greatly different from the original ones, although they are not, strictly speaking, residual clays.[1]

Distribution of residual clays.—Residual clays, usually of ferruginous character, are found in many portions of the United States, but reach their maximum development in that portion lying east of the Mississippi and south of the southern margin of the ice-sheet of the glacial epoch.

North of the terminal moraine they are found only in protected situations (Fig. 3) or non-glaciated areas. Thus, for example, an area of residual clay, derived from limestone, is found in the driftless area of Wisconsin.[2] This is a silty clay in its upper part, and a tough jointed clay below, while scattered through it are numerous cherty fragments.

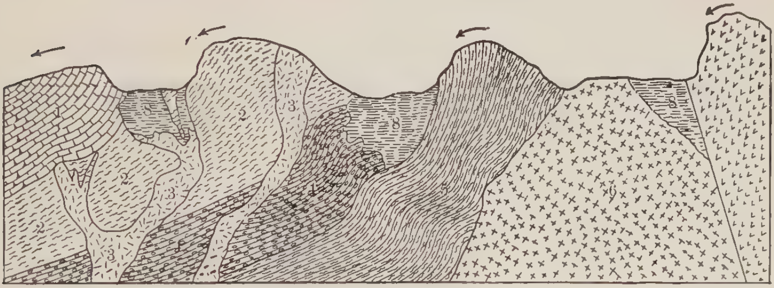

Fig. 3.—Generalized section showing three possible occurrences of kaolin in a glaciated country. 1, limestone; 2, mica schist; 3, pegmatite; 4, feldspathic quartzite; 5, dark gneiss; 6, light granite; 7, dark granite; 8, kaolin, protected from glacial erosion. Arrow indicates direction of ice movement. (After Loughlin, Conn. Geol. and Nat. Hist. Surv., Bull. 4, 1905.)

A second type of residual clay occurring in Wisconsin is that found underlying the Potsdam sandstone and has been derived from the pre-Cambrian crystallines. Several are found in New England. (See Conn. and Mass.)

The general character of these residuals is much the same whatever the parent rock. Nearly all are ferruginous, and contain angular mineral particles, as well as more or less decomposed ones, from which the more soluble constituents have been leached out. The colors range usually from brown or red to yellow. In the Piedmont and Appalachian areas of the Southern States they often attain great thickness and are widely used for brickmaking.[1] In rare cases they are formed from rocks running low in iron, and then the clay is white in color.

---

[1] *Colluvial deposits* of G. P. Merrill.

[2] Chamberlin and Salisbury, 6th Ann. Rep. U. S. Geol. Surv., p. 240, 1885.

The following analyses [2] represent the composition of several residual clays:

ANALYSES OF RESIDUAL CLAYS

Constituents	I	II	III	IV	V	VI	VII	VIII	IX	X
SiO_2	71.13	49.90	53.09	49.13	55.42	40.127	39.55	66.27	77.24	55.39
Al_2O_3	12.50	18.64	21.43	20.08	22.17	13.75	28.76	15.25	26.17	20.16
Fe_2O_3	5.52	17.19	8.53	11.04	8.30	12.315	16.80	6.97	7.76	8.79
FeO	.45	.27	.86	.93						
TiO_2	.45	.28	.16	.13	......	....	.64			
P_2O_5	.02	.03	.03	.04	......	.626	.10	.07	.14	.04
MnO	.04	.01	.03	.06						
CaO	.85	.93	.95	1.22	.15	3.518	.37	.24	.18	.51
MgO	.38	.73	1.43	1.92	1.45	.479	.59	.43	.38	1.27
Na_2O	2.19	.80	1.45	1.33	.17	.006	Tr.	.40	.29	.79
K_2O	1.61	.93	.83	1.60	2.32	.118	Tr.	.86	4.41	4.03
H_2O	*4.63	*10.46	*10.79	*11.72	*9.86	†27.441	13.26	8.2	.....	7.38
CO_2	.43	.30	.29	.39	......	2.251				
C	.19	.34	.22	1.09						
	100.39	100.50	100.09	100.68	99.84	100.631	100.07	98.69	99.27	98.30

* Contains hydrogen and organic matter. Dried at 100° C.
† Contains 11.21 per cent of organic matter.

Numbers I, II, II, and IV are limestone residuals from southern Wisconsin. Nos. I and II are from the same vertical section, I being 4½ feet from the surface, and II 8½, and in contact with the underlying limestone. Nos. III and IV are similarly related, III being 3 feet from the surface, and IV 4½ feet, the lower sample lying on the unchanged rock. "The larger percentages of silica, in samples from nearest surface, are due to higher state of decomposition, the soluble portions having been more largely removed. The presence of larger percentages of alkalies in these same samples indicates that these salts existed in the form of silicates which have resisted the decomposing influences, and remain mechanically included in the residues." No. V represents a residual from the Knox dolomite at Morristown, Ala.; VI is a red earth formed by decay of Bermuda coralline limestone; VII is a diabase residual from Wadesboro, N. C.; VIII a gabbro subsoil from Maryland; IX a Trenton limestone residual from Hagerstown, Md.; and X a Triassic limestone residual.

The texture of some of the above residual soils has been determined as follows: [3]

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[1] G. P. Merrill, Rocks, Rock-weathering, and Soils, p. 301; I. C. Russell, U. S. Geol. Surv., Bull. 52, 1884–85; H. Ries, U. S. Geol. Surv., Prof. Pap. 11.

[2] G. P. Merrill, Rocks, Rock-weathering, and Soils, p. 306.

[3] Whitney, M., Md. Agric. Exp. Sta., Bull. 21, 1893.

MECHANICAL ANALYSES OF RESIDUAL CLAYS

Diameter of particles, mm.	Name	I	II	III	IV	V
2–1	Fine gravel	.54	.17	.00	.00	.19
1–.5	Coarse sand	.32	.00	.23	.26	1.80
.5 –.25	Medium sand	.72	.15	1.29	.18	3.12
.25 –.1	Fine sand	.62	.25	4.03	.66	6.96
.1 –.05	Very fine sand	4.03	2.34	11.57	6.73	8.76
.05 –.01	Silt	36.02	19.04	38.97	47.32	34.92
.01 –.005	Fine silt	14.99	20.88	8.84	10.04	12.14
.005–.0001	Clay	41.24	51.77	32.70	34.90	28.82
	Total mineral matter	88.48	94.60	97.63	94.44	96.71
	Organic matter, water, loss	1.52	5.40	2.37	5.56	3.29
		100.00	100.00	100.00	100.00	100.00

Laterite.—This represents a peculiar type of residual clay formed by the weathering of different kinds of rocks, under conditions yielding a product in which aluminum hydrate and iron hydroxides predominate. This means then that during the process of weathering the silica has been largely eliminated.

Laterite has been derived from a number of different kinds of rock, but the changes which bring about its formation appear to be peculiarly characteristic of the tropics.

The two following analyses show: I, a fresh nepheline syenite, and II the laterite derived from it:

ANALYSES OF SYENITE AND LATERITE

	I	II		I	II
SiO_2	56.88	35.14	MgO	.56	.21
TiO_2	.29	.70	Na_2O	8.30	
Al_2O_3	22.60	40.12	K_2O	5.57	
Fe_2O_3	.97	4.12	P_2O_5	.08	
FeO	2.19		H_2O	.98	17.84
CaO	1.33	.45	Insoluble	.34	1.46

Some laterites are so rich in aluminum hydroxide as to serve as ores of aluminum, while others may be sufficiently rich in iron hydroxide to be used as iron ores. If we consider bauxite as a form of laterite, then its formation cannot be said to be strictly confined to tropical regions.

Numerous papers have been written on laterites, but that by C. O. Swanson, summarizes well our existing knowledge and also contains a bibliography.[1]

Residual Clays Formed by Processes other than Surface Weathering

Clays, often of a non-ferruginous character, which have been formed by the decomposition or alteration of rocks, are sometimes found in such relationships as to throw some doubt on their having originated by the ordinary processes of weathering.

The belief expressed by some is that such deposits have been formed by rising vapors or solutions presumably of igneous origin, but, there are other cases where the exact source of the alteration agent is not known. The view has been strongly argued for by some, but in most cases lacks definite proof.

Clay formation by hydrothermal solutions.—One of the first to advocate a hydrothermal origin for residual clay (kaolin) was von Buch in 1824,[2] who observed that the kaolin at Halle, Germany, was associated with minerals containing fluorine and hence thought it was formed by hydrofluoric acid acting on the granite. This view was decidedly incorrect as one could see that the kaolin passed into porphyry with depth, and hence was a product of weathering.[3]

Daubrée considered that the kaolin near St. Austell in Cornwall,[4] Central France, and the Erzgebirge must have had a similar origin.

The formation of kaolin by other causes than surface agencies has been referred to by B. von Inkey and Semper as a product of propylitization in some cases.[5]

Cross and Penrose [6] suggested a pneumatolytic origin for the kaolin found in some of the Cripple Creek, Colo., mines, but Ransome and Lindgren,[7] have disputed this.

J. H. Collins was a strong advocate of the view that the kaolins of the Cornwall district, England, were of pneumatolytic origin. Here we have some of the deepest known kaolin deposits of the world, which occur in a granite that is traversed by tin veins, and which have been worked to a depth of several hundred feet.

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[1] Jour. Amer. Ceram. Soc., VI, p. 1248, 1923.

[2] Min. Tasch., 1824.

[3] Personal observation by the author, and see also, Selle, V., Zeitschr. f. Naturw., Halle, LXXIX, 1907.

[4] Études synthétiques de Geologie Expérimentale, 1879.

[5] Nagyag u. seine Lagerstätten, Budapest, 1885.

[6] U. S. Geol. Surv., 16th Ann. Rept., Pt. II, p. 160.

[7] U. S. Geol. Surv., Bull. 254, p. 21, 1904.

Collins sought to show that the kaolin had been formed by the action of fluoric vapors on granite, and attempted[1] to prove that this was possible by exposing feldspar to the action of hydrofluoric acid.

The feldspar, according to Collins, was converted into hydrated silicate of alumina, mixed with soluble fluoride of potassium, while pure silica was deposited on the sides of the tube.

With such treatment the orthoclase yielded more readily than either albite or oligoclase. The following analyses show the effect of 96 hours' treatment of orthoclase with hydrofluoric acid at 60° F.:

	I	II	III
Silica (SiO_2)	63.70	49.20	44.10
Alumina (Al_2O_3)	19.76	35.12	40.25
Potash (K_2O)	13.61	.12	.25
Soda (Na_2O)	2.26	Tr.	Tr.
Ferric oxide (Fe_2O_3)	.71	Tr.	Tr.
Water (H_2O)	Tr.	14.20	15.01
	100.04	98.64	99.61

I. The original feldspar.
II. Inner layer of altered feldspar.
III. Outer layer of altered feldspar.

From the analysis it will be seen that the composition of the outer layer simply approximates that of kaolinite.

The artificial clay thus produced, when examined under the microscope, resembled washed kaolin. It showed no hexagonal scales, but contained a number of minute colorless cubes which are supposed to be fluorspar.

If Mr. Collins' theory be correct, the kaolin deposits should extend to great depths, but if the kaolinization be due to weathering, then we should encounter undecomposed felspar at the limit to which weathering has reached. More recently Rösler[2] has advanced the view, on what seems to the writer insufficient evidence, that the kaolinization of feldspars is never due to atmospheric action, but to post-volcanic pneumatolytic and pneumato-hydatogenic processes.[1]

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[1] Min. Mag., 1887, VII, p. 213.

[2] H. Rösler, Beiträge zur kenntniss der Kaolinlagerstätten, Neues Jahrb. f. Min., Geol. u. Pal., XV. Beilage-Band, 2d Heft, pp. 231–393.

In the author's opinion, not one of the seven criteria named by Rösler are positive proof of pneumatolytic origin.[2]

The very fact that many of our kaolins pass into undecomposed rock when the limit of weathering is reached shows the incorrectness of such a broad statement.[3]

In the United States several occurrences of kaolin or kaolinite formation due to ascending hot waters have been suggested in some San Juan ores of the Silverton, Colo., quadrangle,[4] at Boulder Hot Springs, Mont.,[5] and in the ore of the Bassick Mine, Colo.[6]

Ransome states that at Goldfield, Nev., the kaolinite occurs with alunite, gold and sulphides, so intimately mixed as to show that it was formed before and independent of weathering.[7]

The latest described case is that of the kaolin deposits of St. Remi d'Amherst in Quebec, which occur in quartzite. M. E. Wilson in describing these has assigned a hydrothermal origin to them, and claims that the host rock is pure quartzite which could not have yielded kaolin by weathering.[8] The solutions are believed to have risen along fault fractures.

Lindgren [9] in combating the theory of hydrothermal origin asserts that he has never looked upon kaolinite as a high-temperature mineral, but considers it either a result of the alteration of feldspars by descending waters with SO_3 or CO_2, or by weak carbonated ascending waters near the surface. This last point, C. E. Tolman,[10] thinks, lacks proof. The points listed by Lindgren in favor of a low temperature origin are: 1. Kaolinite is a definite hydrated aluminum silicate: 2. Except for the experiment by Collins (see above) it has never been made synthetically. 3. It is decomposed by H_2SO_4. 4. Kaolinite loses some water in exsiccator at 125° C., but most of it at 470–500° C. and a little at red heat. 5. Stremme says that the Al_2O_3 and SiO_2 of kaolinite dissociate at 500° C. 6. Kaolinite absorbs bases as copper from a solution of silicate and gives off a corresponding amount of bases, which Lindgren believes shows that the kaolinite cannot be formed above a temperature of 470° C.

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[1] See also E. Zalinski on the kaolinization of the granite of the turquoise deposits in New Mexico; Econ. Geol., II, p. 479, 1907; Stütze, Zeitschr. prak. Geol., XIII, p. 333, 1905.

[2] See Ries, Origin of Kaolin, Trans. Amer. Ceram. Soc., XIII, p. 51, 1911.

[3] In this connection, see G. P. Merrill, What Constitutes a Clay, Amer. Geol. XXX, Nov. 1902, and H. Ries, Origin of Kaolin, Trans. Amer. Ceramic Soc., II, p. 93, 1900.

[4] Ransome, U. S. Geol. Surv., Bull. 182, p. 73, 1901.

[5] Weed, *ibid.*, 21st Ann. Rept., Pt. 2, p. 253, 1900.

[6] Emmons, S. F., *ibid.*, 17th Ann. Rept., Pt. II, p. 432, 1896.

[7] Econ. Geol., II, p. 690, 1907.

[8] Can. Geol. Surv., Mem. 113, 1919.

[9] Econ. Geol., X, p. 89, 1915; See also Leonard, R. J., Econ. Geol. XXII, p. 18, 1927.

[10] Econ. Geol., IX, p. 200, 1914.

Lemberg (quoted by Stremme) showed that solutions of potassium and sodium salts acting on kaolinite at temperatures of 100°–200° C. change it to alkaline silicates similar to sodalite, nephelite and analcite, some of which are crystalline. From this it is assumed that kaolinite is unstable when heated in strong alkaline solutions from 100°–200° in closed vessels. Since in ore deposition the rising solutions which attack the wall rock are usually hot and strongly alkaline, it would seem to argue against the formation of kaolinite under such conditions, sericite instead being formed.

In many ore bodies kaolinite is found extending down to the water level, but below this the soft white material which is often so abundant is presumably sericite.

If the sericite is exposed to a weak sulphuric acid solution in the zone of weathering it is said to change to kaolinite, on the other hand kaolinite is not stable in a strongly acid solution.

However, in spite of arguments to the contrary, there seems to be strong indications that kaolinite may occasionally be formed by rising thermal solutions. (See further under Kaolinite.)

Residual clays formed by rising carbonated waters.—At Karlsbad, Czechoslovakia, the kaolin deposits are associated with granite, and are thought by some to owe their origin to rising spring waters containing carbon dioxide.[1]

Here according to C. Gagel and H. Stremme the granite is kaolinized around the vent of one of the springs,[2] indeed it was found that the granite was completely altered within a circle having a diameter of 40 m. and a depth of 50 m.

The analyses on p. 16 illustrate these changes.

A. F. Buddington in discussing the occurrence of kaolinite and calcite in miarolitic cavities of a rhyolite porphyry of southeastern Alaska believes that the former has been derived through the partial alteration and leaching of the plagioclase of an underlying granite porphyry by rising thermal carbonated waters of relatively low temperature.[3]

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[1] See Stremme and Grupe, Monatsber. d. d. Geol. Ges., 1910; Gagel and Stremme, Centralbl. f. Min. u. s. w., 1909.

[2] Centralbl. für Min., 1909, pp. 427–437 and 467–475.

[3] Jour. Geol., XXXI, p. 149, 1923.

	I	II	III	IV
SiO_2	71.67	69.87	64.68	49.71
TiO_2	0.14	0.10	Trace	0.10
Al_2O_3	14.64	17.41	24.93	35.20
Fe_2O_3	1.19	0.69	0.46	1.22
FeO	1.08	3.02	0.26	0.21
CaO	0.38	0.20	0.10	0.17
MgO	0.18	0.15	0.06	0.13
K_2O	5.20	0.36	0.29	0.54
Na_2O	3.23	0.16	0.08	0.06
H_2O	1.71	6.33	8.62	12.13
CO_2	None	1.49	....	Trace
SO_3	0.18	0.06	0.13	0.15
P_2O_5	0.24	0.11	0.18	0.12
	99.84	99.95	99.79	99.74

I. Coarse granite 200 meters from the spring.
II. Kaolinized coarse granite at spring outlet, depth about 50 meters.
III. Kaolinized fine granite (aplite) at spring outlet, depth about 50 meters.
IV. Finest washings from II and III (nearly pure kaolinite).

Deposits formed by downward moving sulphate solutions.—Lindgren and Loughlin,[1] in their report on the Ore Deposits of the Tintic District, note the occurrence of irregular bodies of limonite, kaolin, and jasperoid along the contact of limestone and monzonite. A volcanic rock overlies the limestone, and the former is believed to have been altered to a quartz-sericite-pyrite aggregate by rising solutions. Later the pyritic volcanic rocks were oxidized by surface waters, with the formation of $FeSO_4$ and H_2SO_4. The latter is thought to have attacked the sericite, converting it in part to soluble alumina and silica, and leaving insoluble kaolinite behind. Some of this kaolinite may have been carried downward with H_2SO_4 which attacked the limestone, and brought about a replacement of the calcium carbonate by kaolinite.

Other cases involving the action of sulphate solutions have been noted by Parsons,[2] Ransome,[3] and Jaquet.[4]

Residual clays formed indirectly[5] **by meteoric waters.**—A deposit of this type and the only representative of this class so far as known is the so-called Indianaite of Indiana.

[1] U. S. Geol. Surv., Prof. Pap. 107, p. 262.

[2] Ont. Bur. Mines, XXIV, Pt. I, p. 185, 1915.

[3] Econ. Geol., II, p. 689, 1907.

[4] Report on Broken Hill Lode, New South Wales, 1894, p. 89.

[5] Logan, W. N., U. S. Geol. Surv., Bull. 708, p. 147, 1922, and Ries, H., *ibid.*, p. 154; Logan, Ind., State Dept. Conserv., Bull. 6, 1920. See under Indiana.

This clay which is found in the lower part of the Mansfield sandstone near its contact with the underlying Chester shale, appears without doubt to have resulted from the replacement of the quartz grains and pebbles by alumina-bearing solutions, which were derived from the underlying Chester shale, which supplied aluminum sulphate. Logan believes that bacteria played a role in the process, but Ries does not consider this necessary. (See under Indiana and Indianaite.)

As bearing on the deposition of kaolinite by surface waters below the oxidized zone it will be of interest to quote G. F. Loughlin.[1] He states:

"The kaolin in certain sulphide ores in the Leadville (Colo.) district . . . has been noted in different parts of the district but the most interesting occurrences were found in the Golden Eagle mine, Breece Hill. The sulphides, principally pyrite and chalcopyrite, are either tarnished or coated with films of chalcocite, or are free from any sign of alteration; but the original gangue, manganosiderite is almost completely replaced by kaolin. Where replacement is complete the sulphides show no evidence whatever of mechanical disturbance and in part no evidence of chemical reaction. Where the sulphides are coated with chalcocite the chalcocite has been deposited later than the kaolin, and apparently represents a later stage of alteration. . . . Certain beds of the white limestone are also replaced by kaolin." He believes that water descending through the pyritic porphyry dissolved alumina and silica and carried them to or below the water level, where conditions favored the replacement of carbonates by kaolinite.

TRANSPORTED CLAYS

SEDIMENTARY CLAYS

Origin.—As mentioned above, residual clays rarely remain on steep slopes, but are carried by rain wash into streams and transported by these to lower and sometimes distant areas. By this means residual clays possibly of different character may be washed down into the same stream and become mixed together. This process of wash and transportation can be seen in any abandoned clay bank, where the clay of the slopes is washed down and spread out over the bottom of the pit.

As long as the stream maintains its velocity it will carry the clay in suspension, but if its velocity be checked, so that the water becomes quiet and free from currents, the particles begin to settle on the bottom, forming a clay layer of variable extent and thickness. This may be added to from time to time, and to such a deposit the name of sedimen-

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[1] Econ. Geol., XIX, p. 70, 1924.

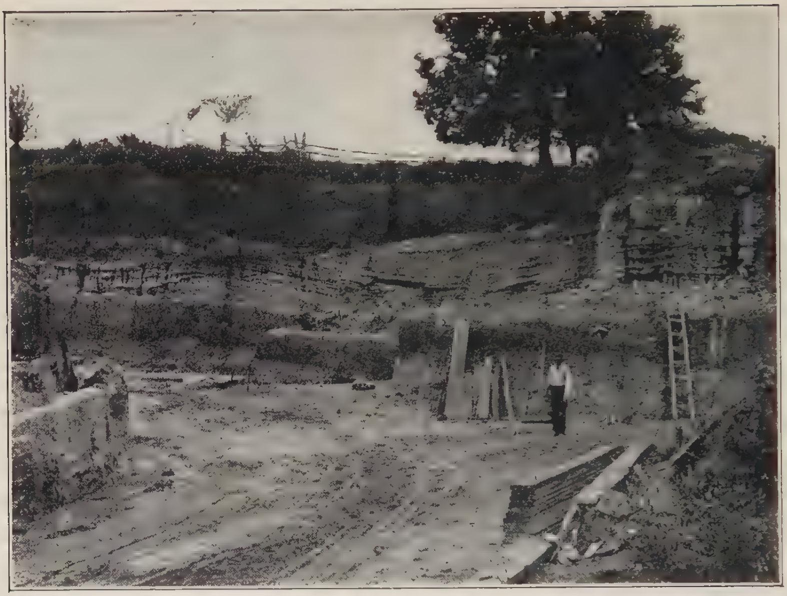

Fig. 4.—Section showing beds of stratified clay overlain by glacial drift. (After Ries, N. J. Geol. Surv., Fin. Rept., VI, 1904.)

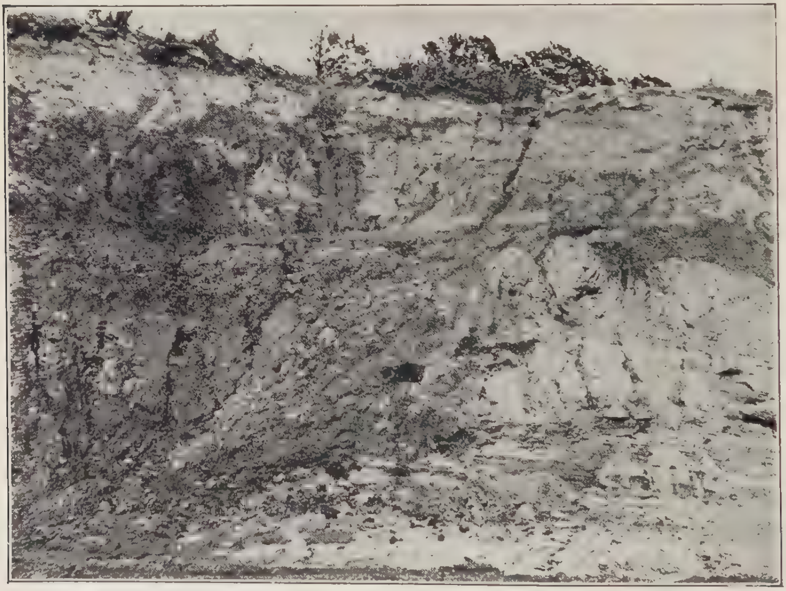

Fig. 5.—Bank of clay showing white sand on right, passing into a black clay on the left. (After Ries, N. J. Geol. Surv., Fin. Rept., VI, 1904.)

tary clay is applied. All sedimentary clays are more or less distinctly stratified or made up of layers, this being due to the fact that one layer of sediment is laid down on top of another (Fig. 4). If there were absolutely no difference in the character of the material deposited, it would form one thick homogeneous bed, but there is usually more or less variation, a layer of very fine material being laid down at one time and a layer of coarser material on top of it, or vice versa. These layers may also vary in thickness, and since there is less cohesion between unlike particles, the two layers will tend to separate along their line of contact.

As the finer material can only be deposited in quiet water, and coarse material in disturbed waters, so from the character of the deposit we can read much regarding the conditions under which it was formed. If, therefore, in the same bank alternating layers of sand, clay, and gravel are found, it indicates a change from disturbed to quiet water, and still later rapid currents over the spot in which these materials were deposited. The commonest evidence of current deposition is seen in the cross-bedded structure of some sand beds where the layers dip in many different directions, due to shifting currents which have deposited the sand in inclined layers. The beds of thinly stratified or laminated sands and clays found in many of the Cretaceous and Tertiary deposits of the coastal plain are another example of rapid changes in the conditions of deposition.

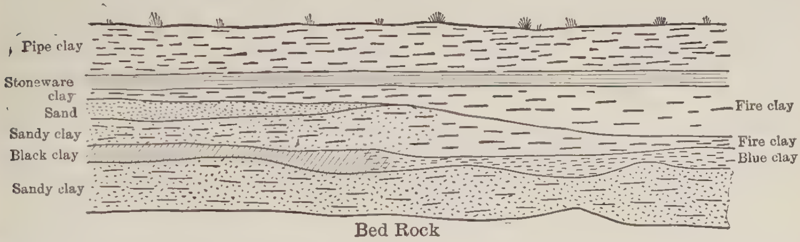

FIG. 6.—Generalized section showing how clay beds may vary both vertically and horizontally.

Sedimentary clays can be distinguished from residual clays chiefly by their stratification, and also by the fact that they commonly bear no direct relation to the underlying rock on which they may rest.

Structural irregularities in sedimentary clays.—All sedimentary clays resemble each other in being stratified, but, aside from this, they may show marked irregularities in structure.

Thus, any one bed, if followed from point to point, may show variations in thickness, pinching or narrowing in one place and thickening or swelling in others, as shown in Fig. 6.

In digging clay the miner often finds streaks of sand extending through the deposit and cutting through several different layers, these having been caused by the filling of channels cut in the clay deposits by streams after the elevation of the former to dry land. Occasionally a bed of clay may be extensively worn away or corraded by currents subsequent to its deposition, leaving its upper surface very uneven, and on this an entirely different kind of material may be deposited, covering the earlier bed, and filling the depressions in its surface. If the erosion has been deep, adjoining pits dug at the same level may find clay in one case and sand in the other (Fig. 7). Such irregularities are known to occur in both clays and shales.

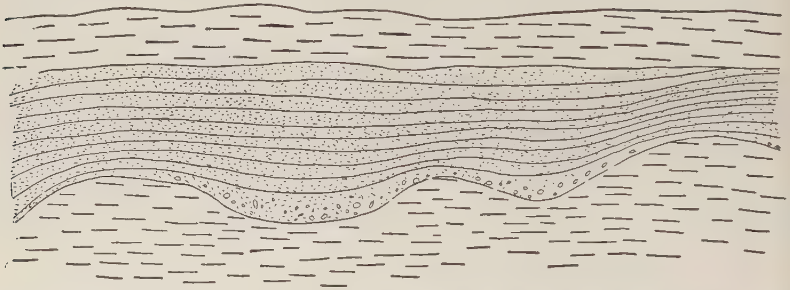

Fig. 7.—Section showing uneven boundary of two clay beds, due to erosion of one before deposition of the other.

While in many instances the changes in the deposit are clearly visible to the naked eye, variations may also occur, due to the same cause, which would only show on burning. Thus, for example, the so-called retort-clay, found in the Woodbridge region of New Jersey, is similar in its plastic qualties wherever found, but the shrinkage of that found in the different pits is not always the same, because it varies in fineness from place to place. It may also vary in color.

CLASSIFICATION OF SEDIMENTARY CLAYS

The general character of sedimentary clays is more or less influenced by the locality and conditions of deposition, which enables us, therefore, to divide them into the following classes:

Marine clays.—This class includes those sedimentary clays deposited on the ocean bottom, where the water is quiet. They have, therefore, been laid down at some distance from the shore, since nearer the land, where the water is shallower and disturbed, only coarser materials can be deposited. Beds of clay of this type may be of vast extent and great thickness, but will naturally show some variation, horizontally at least, because the different rivers flowing into the sea usually bring down different classes of material.

Thus, one stream may carry the wash from an area of iron-stained clay, and another the drainage from an area of white or light-colored clay. As a sediment spread out over the bottom, the areas of deposition might overlap, and there would thus be formed an intermediate zone made up of a mixture of the two sediments. This would show itself later as horizontal transition from one kind of clay to another. These changes may occur gradually, or at other times within the distance of a few feet (Fig. 5).

The laminations produced by vertical changes are shown in Fig. 4.

The most persistent beds of this class are found in the rocks of the Silurian, Devonian, and Carboniferous systems, but beds of considerable horizontal extent are at times found in the Mesozoic formations.[1]

Estuarine clays.—These form a second type of some importance in certain areas. They represent bodies of clay laid down in shallow arms of the sea, and are consequently found in areas that are comparatively long and narrow, with the deposits showing a tendency towards basin shapes. If strong currents enter the estuary from its upper end, the settling of the clay mud may be prevented, except in areas of quiet water in recesses of the bay shore. Or, if the estuary is supplied by one stream at its head, and this of low velocity, the finer clays will be found at a point most distant from the mouth of the river. In such cases we should anticipate an increase in coarseness of the clay bed or series of beds as they are followed from what was formerly the old shore line up to the mouth of the former river that brought down the sediment.

Estuarine clays often show sandy laminations, and are not infrequently associated with shore marshes, due to the gradual filling up of the estuary and the growth of plants on the mud flats thus formed. The clays of the Hackensack region of New Jersey and those of the Hudson Valley of New York (in part) are examples of estuarine deposits, formed at the close of the glacial period, when the region around the Palisades stood somewhat lower in respect to sea-level than at present.[1]

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[1] A peculiar type of marine deposit, which covers many square miles of the deeper lying portions of the ocean floor, is the so-called *Red Clay*. It is of no economic value.

The composite analysis of a number of samples, recalculated so as to omit adsorbed sea-salts, calcium carbonate, and a little gypsum, is given by Clarke (Jour. Geol., XV, p. 787) as follows: SiO_2, 54.48; TiO_2, 0.98; Al_2O_3, 15.94; Cr_2O_3, 0.012; Fe_2O_3, 8.66; FeO, 0.84; NiO,CoO, 0.039; MnO_2, 1.21; MgO, 3.31; CaO, 1.96; SrO, 0.056; BaO, 0.20; K_2O, 2.85; Na_2O, 2.05; V_2O_3, 0.035; As_2O_3, 0.001; MoO_3, tr.; P_2O_5, 0.30; CuO, 0.024; PbO, 0.008; ZnO, 0.005; H_2O, 7.04; 100.00.

Swamp and lake clays.—Swamp and lake clays constitute a third class of deposits, which have been formed in basin-shaped depressions occupied by lakes or swamps. They represent a common type, of variable extent and thickness, but all agree in being more or less basin-shaped. They not infrequently show alternating beds of clay and sand, the latter in such thin laminæ as to be readily overlooked, but causing the clay layers to split apart easily. Many of the lake clays are directly or indirectly of glacial origin, having been laid down in basins or hollows along the margin of the continental ice-sheet, or else in valleys that have been dammed up by the accumulation of a mass of drift across them. They are usually surface deposits, of variable thickness, often highly plastic, and more or less impure. Their chief use is for common brick and earthenware, and they are rarely of refractory character.

Some lake clays show a characteristic banding (*varves*), representing seasonal accumulations.[2]

Those formed at earlier geologic periods may have become subsequently covered by other sediments, as may of the coal under clays of the Carboniferous. These sometimes show the upright stumps of trees that grew in the swamp in which the clay was deposited, and are referred to in more detail on p. 29.

Flood-plain and terrace clays.—Many rivers, especially in broad valleys, are bordered by a terrace or plain, there being sometimes two or more, extending like a series of shelves, or steps, up the valley side. The lowest of these is often covered by the river during periods of high water, and is consequently termed the flood-plain. In such times much clayey sediment is added to the surface of this flood-terrace, and thus a flood-plain clay deposit may be built up. (Figs. 12 and 13.)

Owing to the fact that there is usually some current setting along over the plain when it is overflowed, the finest sediments cannot settle down, except in protected spots, and consequently most terrace clays are rather sandy, with here and there pockets of fine, plastic clay. They also frequently contain more or less organic matter. Along its inner edge the terrace may be covered by a mixture of clay, sand, and stones, washed down from neighboring slopes.

Where several terraces are found it indicates that the stream was formerly at the higher levels, and has cut down its bed, each terrace

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[1] Report on Glacial Geology, N. J. Geol. Survey, Vol. V, p. 196; and N. Y. State Museum, Bull. 35, p. 576.

[2] Antevs, E., Can. Geol. Surv., Mem. 146, 1925, (has bibliography); Reeds, C. A., Amer. Mus. Nov., No. 209, Feb. 1926.

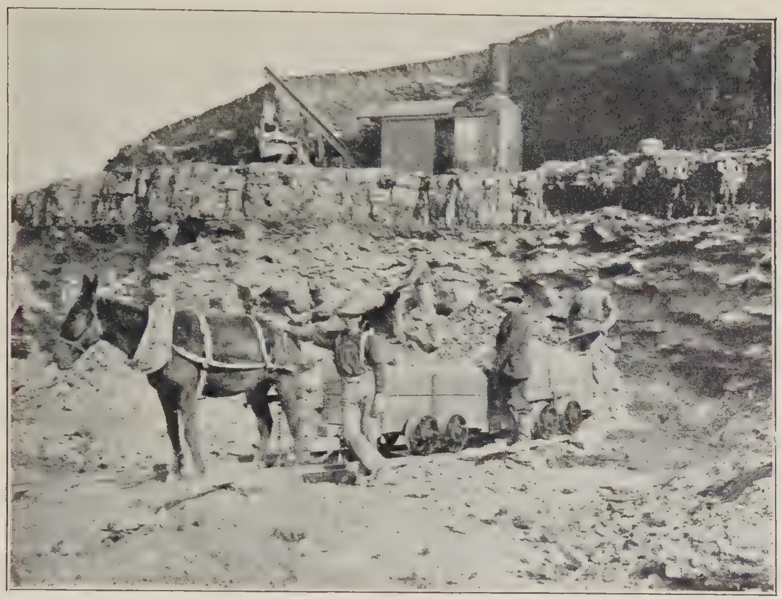

FIG. 8.—Section showing fire-clay underlying coal-seam. The upper clay above coal is of impure character. (Photo loaned by Robinson Clay-product Company.)

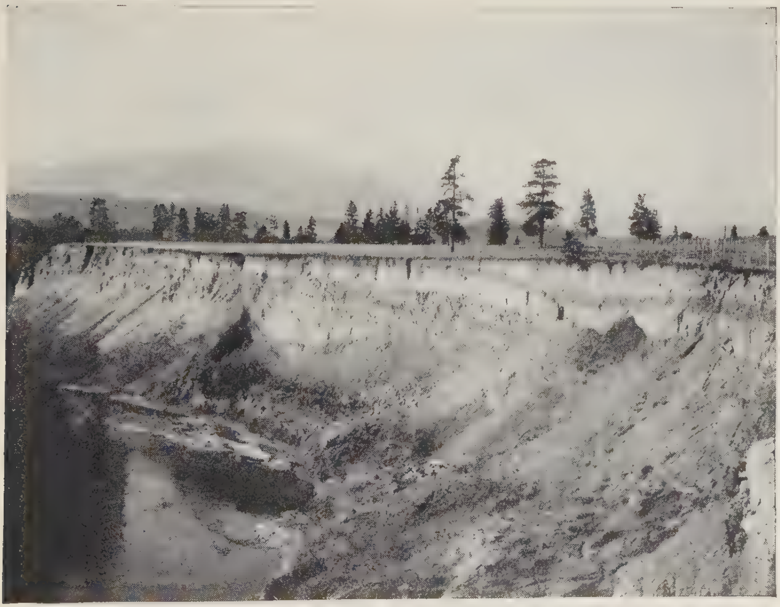

FIG. 9.—Deposit of lake clay in Nicola Valley, Brit. Col. (H. Ries, Photo.)

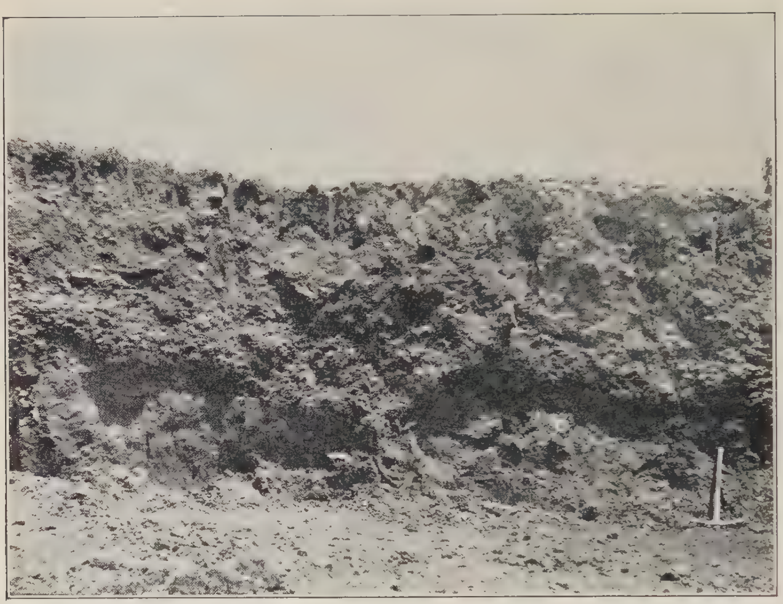

Fig. 10.—Deposit of stony glacial clay. (After H. Ries, N. J. Geol. Surv., Fin. Rept., VI.)

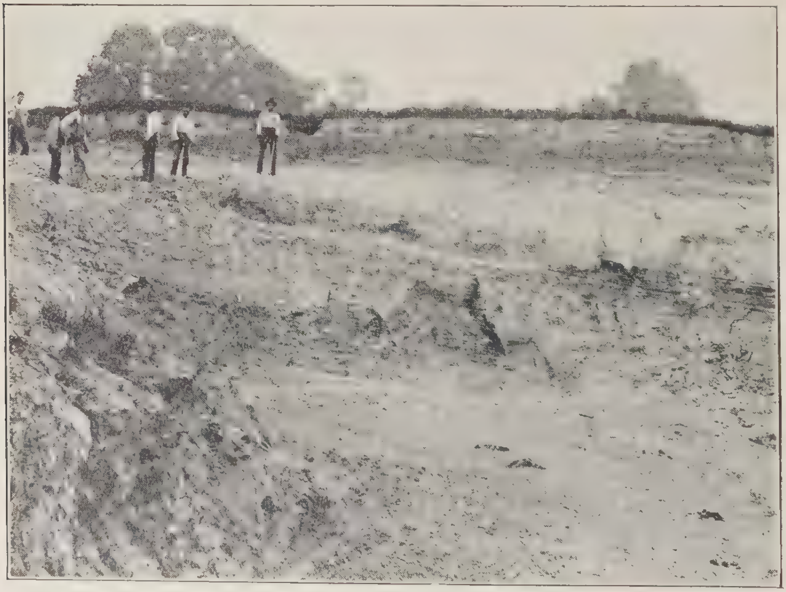

Fig. 11.—Clay pit in Lignitic Tertiary formation, Athens, Tex. Shows gently dipping layers. (Photo by H. Ries, 1903.)

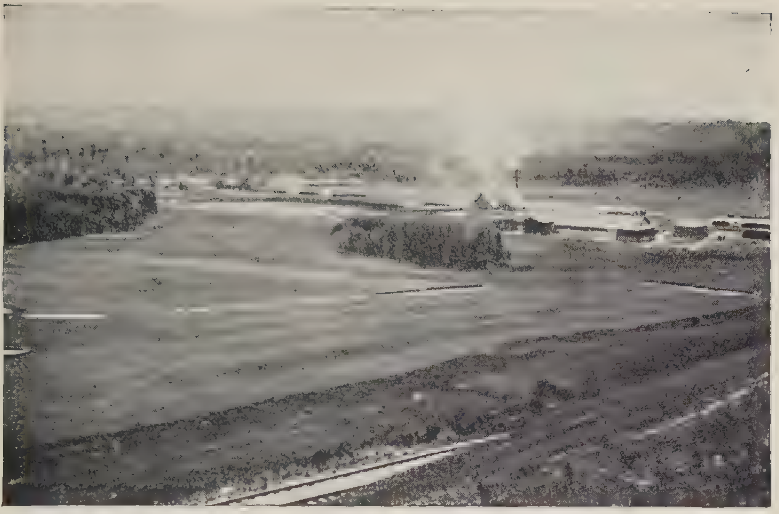

Fig. 12.—Flood plain terrace underlain with clay, along Saskatchewan River, Edmonton, Alta. (H. Ries., photo, Can. Geol. Surv., Mem. 24-E.)

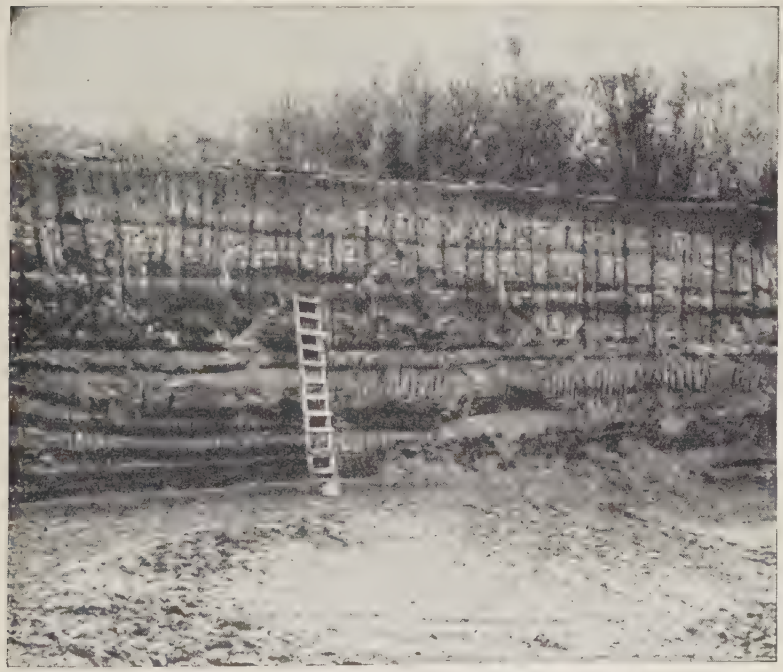

Fig. 13.—Section through the deposit shown in Fig. 12, with light sandy beds, and darker clayey ones.

representing a former flood-plain. Even along the same stream, however, the clays of the several terraces may vary widely in their character, those of one terrace being perhaps suitable for pottery, and those of the second being available only for common brick and tile. Examples of such clays are to be found in many regions.

Flood plain deposits may show considerable irregularity, gradations between clay, sand and gravel being not uncommon.

Delta clays.—These are supposed to have been deposited in quiet water near the mouths of rivers, or as basins on the surface of deltas. Relatively few deposits of this character have been described, and while they probably in most cases would be silty and impure, still occasionally some interesting deposits of this type occur as in the Eocene delta of the Frazer River in British Columbia.[1]

Drift or bowlder clays.—In that portion of the United States formerly covered by the continental ice-sheet there are occasional deposits of clay formed directly by the glacier. These are usually tough, dense, gritty clays, often containing many stones (Fig. 10). The material, till, deposited by the ice, is usually too stony and sandy to serve as clay, although often known as bowlder clay. Locally, however, although the ice-transported material has been largely ground to a fine rock flour, the bowlder clay is plastic enough and not too full of stones for use. Such deposits are mostly of limited extent, impure, and of little value.

In addition to this type of clay formed directly by the ice, there were clays deposited in lakes or along flood-plains by the streams issuing from the glacier. These were composed of material derived from the ice, but since they were deposited by water they were stratified, and may properly be classed as lacustrine, estuarine, or flood-plain of glacial age. Bowlder clays, although abundantly distributed, are often too stony to be of much value for the manufacture of clay products.

Æolian clays.—In many parts of the West there is found a silty, often calcareous clay, termed the loess. This, although commonly a water deposit, may at times have been formed by wind action. It could therefore properly be classed as transported clay, and would also show a stratified structure.

Chemical deposits.—One of the most puzzling types of clay is that known as flint clay, which is usually high in alumina, with a very fine texture and conchoidal fracture.

In many cases the material is of such remarkably fine texture as to prevent a mineralogical diagnosis with the microscope, but its composition may suggest the presence of a large amount of some hydrous aluminum silicate such as kaolinite.

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[1] Ries and Keele, Can. Geol. Surv., Mem. 24–E, p. 126, 1912; Burwash, Geology of Vancouver and vicinity, 1918.

Occasionally the flint clay may contain oolitic bodies, which when examined under the microscope are found to be composed of diaspore [1] as in the Missouri flint clays, or gibbsite [2] as in those of Kentucky.

Galpin has suggested that the material of flint clay was originally deposited as a colloidal sediment, " whose consolidation took place partly as the settling of a colloidal gel, but mainly as a recrystallization of their hydrous aluminum silicates, with the formation of minute interlocking crystals of kaolinite and hydrated micas, resulting in the formation of flint clays."

There may be some doubt as to whether these are strictly speaking chemical deposits.

Fire-clays of coal measures.—Fire-clays are found in a number of places underlying beds of coal, or at least in the same series with them, and the origin of these " under-clays " has always been a fruitful source of discussion. Clays of a refractory character underlying coal are found in Pennsylvania, Ohio, Maryland, West Virginia, Illinois and Indiana. None are found under coals in Virginia, Michigan, Alabama, Iowa or Arkansas, and even in those states where such clays occur, all of the under-clays are not by any means refractory. The fire-clays themselves may be underlain by shale, sandstone, conglomerate, limestone, or even other beds of coal. The beds rarely show distinct bedding or lamination, and are often lens shaped. No definite relation exists between the refractoriness of the clay and its thickness, or the quality of the coal with which it is associated. It is sometimes noticed that where the under-clay is thick the coal may be thin, or the reverse.

While most of the fire-clays are plastic, beds of flint clay are sometimes present, and when the two occur in the same deposit they exhibit no definite relation to each other.

In the Pennsylvanian system of rocks, nearly all of the fire-clays are found in the lower part, that is in the Pottsville and Allegheny series, while in the southern part of the Appalachian coal field they appear to occur in the Pottsville only.

Various theories have been suggested to explain the origin of the coal-measures fire-clays.

Among the earliest was that of Worthen,[3] who spoke of them as the soil in which the coal-forming plants grew. While it is true that in many under-clays we find roots, known as *Stigmaria*, which belonged to the trees that grew in the old peat swamp, still it is known that many modern peat bogs have no such underclays.

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[1] Somers, U. S. Geol. Surv., Bull. 708, p. 299, 1922. Wherry, Amer. Mineral., III, p. 154, 1918.

[2] Galpin, Trans. Amer. Ceram. Soc., XIV, p. 301, 1912.

[3] Ill. Geol. Surv., I, 1866.

Lesley at a later date[1] expressed the belief that the ponds in which peat accumulated were surrounded by sand and that the water percolating through this into the open water carried only the finest mud. It is questionable whether very much clay could float in in this manner.

Some time later H. A. Wheeler[2] advanced the view that the refractory character of the under-clay was due to plant roots removing the impurities by absorption into their tissues. This is a view that has been widely held, and seems to have much evidence against it. It is difficult to see how this process should so completely purify the clay; moreover in the case of very thick clays the upper portion should be purer than the lower part, which is not always the case, and furthermore some impure clays are found under thick coals, and some of high purity under thin ones.

While T. C. Hopkins[3] expressed somewhat similar views to Wheeler, he suggested that organic acids reduce the iron and render it more soluble. If then seepage is away from the bog, the iron may be carried off, but if towards it the iron may be deposited in the bog as ore. This theory, however, does not explain the formation of fire-clays with little or no vegetable matter over them to supply organic acids.

A somewhat distinct theory is that of Arber,[4] who thinks that the under-clays are marine and brackish water oozes laid down in estuaries, but this does not explain why they are found associated only with coal.

Still a different theory is that of J. J. Stevenson, who regarded the fire-clays as the weathering products of rocks (residual soils) which had been washed into the coal swamps and deposited with humus.[5]

It seems quite evident that few of these theories have appealed to many, and so others have appeared.

A striking one is that proposed by W. Stout.[6] His idea, to endeavor to state it briefly, is that the fire-clays represent the mineral residue left by the oxidation of beds of vegetable matter. He points to what he regards as the constancy of composition of fire-clays at different horizons in the coal measures, and says that their $SiO_2 : Al_2O_3$ ratio approaches that of kaolinite; furthermore, that the ash of pure coals shows a similarity in its percentage of kaolinite. The loss of a few per cent of fluxes in coal ash might in his opinion be easily caused by leaching. To sum up he says that fire-clays " were formed in swamps when plant remains underwent complete oxidation, and peat accumulated in those periods when vegetable tissue was present." Hence according to him there was no break in plant growth, but an alternation of oxidation and coal-forming periods. He admits that some sediment may have been washed into the bogs.

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[1] Sec. Geol. Surv. Pa., Lawrence Co., 1878.

[2] Mo. Geol. Surv., XI, 1896.

[3] Amer. Geol., XXVIII, p. 47, 1901.

[4] Natural History of Coal, p. 91, 1912.

[5] Proc. Amer. Phil. Soc., L, 1911; LI, 1912; LII, 1913.

[6] Trans. Amer. Ceram. Soc., II, p. 557, and Ohio Geol. Surv., Bull. 26.

There seem to be several difficulties with this theory. In the first place it would call for a tremendous thickness of vegetation to yield a thick bed of fire-clay. Secondly, if the land was elevated, it is not quite clear why the plant ash would not be removed by erosion. Third, fire-clays can hardly be said to show such a wide-spread similarity in composition to kaolinite, and flint-clays often deviate appreciably from it. Fourth, it is not clear how wide-spread swamp conditions could exist with complete oxidation going on. Fifth, it would not account for stratified under-clays. Sixth, it seems difficult to explain the complete elimination of all organic matter from the clay. Seventh, if the theory is correct should not fire-clays occur under at least most coals?

Lovejoy,[1] in seeking to find a satisfactory explanation, thinks that the vegetation of the coal basin formed at first a fringe around it, and also occupied islands within it, and that the fire-clay beds represent sediment washed out into the basin in advance of the encroaching vegetation. The fire-clay sediment, according to Lovejoy, has gone through the swamp belt and been purified. Its flocculent nature has resulted in its slowly settling down without developing stratification.

Of all the theories advanced, it seems to the author that Lovejoy's comes nearest to being correct. There is no doubt that the waters of a coal plant swamp must have been rather strongly charged with organic acids, which might serve to purify the fine-grained sediment slowly filtering in to the basin.

The nature of flint-clays is so different from the plastic ones as to call for some special explanation. While several authors have referred to them, perhaps the most detailed work is that of S. L. Galpin,[2] who believed that the flint-clays were recrystallized fine sediments. He thought that they were deposited in colloidal form, and purified by CO_2-bearing waters which transported them into the basins where they were deposited. After deposition as colloidal material, it is supposed that they were recrystallized into kaolinite and hydromica.

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[1] Jour. Amer. Ceram. Soc., VIII, p. 756, 1925.

[2] Studies of flint clays and their associates, Trans. Amer. Ceram. Soc., XIV, p. 301, 1912.

The semi-flint Galpin considers to have been derived from flint-clay by pressure and heat, but this is difficult to understand, since the several types of clay may be so irregularly distributed in the one deposit.

CLASSIFICATION OF CLAY DEPOSITS

Clays may be classified according to their origin, chemical and physical properties, or uses. To the geologist the first is, perhaps, the most important, to the technologist the second and third are of more interest.

Several such classifications have appeared in the United States in the last few years, most of them based primarily on genetic features, and sometimes secondarily on the properties of the clay. They include the following:

Orton's classification.[1]

High-grade clays. (50 per cent or more kaolin) with silica.	1. Kaolin.
	2. China-clay.
	3. Porcelain-clay.
	4. Fire-clay (hard).
	5. Fire-clay (plastic).
	6. Potter's clay.
Low-grade clays. (10 to 70 per cent kaolin with notable per cent fluxing elements.)	1. Argillaceous shale—Paving-block.
	2. Ferruginous shale—Pressed brick.
	3. Siliceous clays—Sewer-pipe and paving-block.
	4. Tile-clays.
	5. Brick-clays.
	6. Calcareous shales—Brick.

Quality is made the basis of division in the above. Nos. 1, 2, and 4 of the first group are practically the same, and the subdivisions of group 2 are not always distinct. The term kaolin is used incorrectly, kaolinite being intended instead.

Wheeler's classification.[2]

1. Whiteware clays.
   - Kaolin.
   - China-clay.
   - Ball-clay.

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[1] Ohio Geol. Surv., VII, p. 52.

[2] Mo. Geol. Surv., XI, p. 25, 1897.

2. Refractory clays.
    - Plastic fire-clay.
    - Flint-clay.
    - Refractory shale.
3. Pottery-clays.
4. Vitrifying clays.
    - Paving-brick clay and shale.
    - Sewer-pipe clay and shale.
    - Roofing-tile clay and shale.
5. Brick-clays.
    - Common-brick clay and shale.
    - Terra-cotta clay and shale.
    - Drain-tile clay and shale.
6. Gumbo clays—Burnt-ballast clay.
7. Slip-clays.

The qualities or uses of the materials are here again employed as bases for subdivision.

Such a classification is somewhat unsatisfactory, for the reason that one kind of clay might be used for several purposes.

Ladd's classification.[1]

Indigenous.
  A. Kaolins.
    (*a*) Superficial sheets.
    (*b*) Pockets.
    (*c*) Veins.

Foreign or transported.
  A. Sedimentary.
    (*a*) Marine.
      1. Pelagic (deposited in deeper water).
      2. Littoral (deposited near shore).
    (*b*) Lacustrine (deposited in fresh-water lakes).
    (*c*) Stream.
      1. Flood-plain.
      2. Delta.
  B. Meta-sedimentary.
  C. Residual.
  D. Unassorted.

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[1] Ga. Geol. Surv., Bull. 6 A, p. 12, 1898.

Under the Indigenous are included those clays formed by the decay of feldspar and other aluminous silicates in place. The Foreign or transported embrace all sedimentary deposits. The meta-sedimentary clays are chemical products resulting from the decomposition of other transported materials, such as volcanic tuffs, pumice, etc. The residual clays include the insoluble residue left by the dissolving of limestones, while under unassorted are included the glacial ones.

The term kaolin, as here used, includes all residual clays, except those derived from limestones, and, since it is not restricted to white-burning ones, its use is unfortunate. Furthermore, the placing of limestone residuals in a separate class seems a rather fine distinction. Delta clays hardly seem of sufficient importance to warrant being placed in a separate class, and are rare.

Buckley's classification.[1]

I. Residual derived from
  A. Granitic or Gneissoid Rocks.
  B. Basic igneous rocks.
  C. Limestone or dolomite.
  D. Slate or shale.
  E. Sandstone.

II. Transported by
  A. Gravity assisted by water.
    Deposits near the heads and along the slopes of ravines.
  B. Ice.
    Deposits resulting mainly from the melting of the ice of the glacial epoch.
  C. Water.
    Marine.
    Lacustrine.
    Stream.
  D. Wind.
    Loess.

E. Orton, Jr.'s classification.[2]

A. Primary or residual clays.
  I. Entirely decomposed feldspathic rock.
    Kaolin or china-clay.

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[1] Wis. Geol. Surv., Bull. VII, Pt. I, p. 14.

[2] Quoted by Beyer and Williams, Ia. Geol. Surv., XIV, p. 40, 1904.

- II. Partially decomposed feldspathic rock.
  - English Cornwall stone.
  - Porzellanerde of the Germans.
- B. Secondary or transported clays.
  - I. Deposited in still water.
    - (*a*) Fire-clays.
      - Highly refractory.
        - Flint fire-clay.
        - Plastic fire-clay.
      - Moderately refractory.
        - No. 2 fire-clay.
        - Stoneware-clay.
        - Sewer-pipe clay.
    - (*b*) Shales.
      - Slaty shales.
      - Bituminous shales.
      - Clay shales.
  - II. Deposited from running water.
    - Alluvium.
    - Sandy clay.
    - Loam.
  - III. Deposited by glacial action.
    - Leached—Whitish or red bowlder clay.
    - Unleached—Blue bowlder clay.
  - IV. Deposited by winds.
    - Loess.

Grimsley and Grout's classification.[1]

- I. Residual clays.
  - 1. Kaolin.
  - 2. China- or porcelain-clay.
- II. Transported clays.
  - A. Refractory (fluxing impurities low).
    - 3. Flint fire-clay.
    - 4. Plastic fire-clay.
  - B. Semi-refractory clay (fluxing impurities medium).
    - 5. Paving-brick clay and shale.
    - 6. Sewer-pipe clay and shale.
    - 7. Roofing-tile clay and shale.
    - 8. Stoneware-clay and shale.

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[1] W. Va. Geol. Surv., Vol. III, p. 70, 1906.

C. Non-refractory (fluxing impurities high).
9. Pottery clay.
(*a*) Ball-clay.
(*b*) Flower-pot clay.
10. Brick- and tile-clay and shale.
(*a*) Ornamental brick-clay and shale.
(*b*) Terra-cotta clay and shale.
(*c*) Ornamental tile-clay and shale.
(*d*) Common-brick and tile-clay and shale.
11. Gumbo ballast-clay.
12. Slip-clay.

Ries' classification.—The following is a modification of a classification suggested by the writer some years ago:[1]

A. Residual clays. Formed in place by rock alteration due to various agents, of either surface or deep-seated origin.

I. Those formed by surface weathering, the processes involving solution, disintegration, or decomposition of silicates.

(*a*) Kaolins, white in color and usually white burning.

PARENT ROCK	SHAPE
Granite, Pegmatite, Rhyolite, Limestone, Shale, Feldspathic Quartzite, Gneiss, Schist, etc.	Blankets; tabular steeply dipping masses; pockets or lenses.

(*b*) Ferruginous clays, derived from different kinds of rocks.

II. White residual clays formed by the action of ascending waters possibly of igneous origin.
(*a*) Formed by rising carbonated waters.
(*b*) Formed by sulphate solutions.

III. Residual clays formed by action of downward moving sulphate solutions.

IV. White residual clays formed by replacement, due to action of waters supposedly of meteoric origin (Indianaite).

B. Colluvial clays, representing deposits formed by wash from the foregoing and of either refractory or non-refractory character.

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[1] Md. Geol. Surv., IV, p. 265, 1902.

C. Transported clays.
- I. Deposited in water.
  - (*a*) Marine clays or shales. Deposits often of great extent.
    - White-burning clays. Ball-clays.
    - Fire-clays or shales. Buff burning.
    - Impure clays or shales.
      - Calcareous.
      - Non-calcareous.
  - (*b*) Lacustrine clays. (Deposited in lakes or swamps.)
    - Fire-clays or shales.
    - Impure clays or shales, red-burning.
    - Calcareous clays, usually of surface character.
  - (*c*) Flood-plain clays.
    - Usually impure and sandy.
  - (*d*) Estuarine clays. (Deposited in estuaries.)
    - Mostly impure and finely laminated.
  - (*e*) Delta clays.
- II. Glacial clays, found in the drift, and often stony.
  - May be either red- or cream-burning.
- III. Wind-formed deposits (some loess).
- IV. Chemical deposits. (Some flint-clays.)

SECONDARY CHANGES IN CLAY DEPOSITS

Changes often take place in clays subsequent to their deposition. These may be local or wide-spread, and in many cases either greatly improve the deposit or render it worthless. The marked effect of some of these changes is often well seen in some clay beds of which only a portion has been altered. These secondary changes are of two kinds, viz., mechanical and chemical.

MECHANICAL CHANGES

Tilting, folding, faulting.—In the uplifting of beds of clay or shale, subsequent to their deposition, the amount of elevation is rarely the same at all points over a large area, so that the beds frequently show a variable degree of tilting. If the uplift is accompanied by folding of the rocks, the dip of the beds may be quite steep. Thus, for example, the Cretaceous and Tertiary clay-bearing formations of the Atlantic and Gulf coastal plain show a dip to the southeast and south respectively (Fig. 11), while the Devonian shales of southern New York dip to the south. At Golden, Colo. (Fig. 106), the beds of Cretaceous fire-clays often have a dip of as much as 90°. Beds of clay and shale sometimes show folds or undulations. In the case of consolidated, or hard beds these may be due to lateral pressure, caused by movements in the earth's crust, while in soft beds the cause is frequently local. Many clay deposits in the Northern States show a local folding caused by the shoving action of the ice-sheet during the glacial period.[1] Such folds, however, are of minor account and affect only a few beds.

Where beds of clay are gently folded into arches (anticlinal folds), Fig. 14, and troughs (synclinal folds), each bed slopes or dips away from the axis of an anticlinal fold and towards the axis of a synclinal fold, but if followed parallel to the axis it will remain at the same level, provided the axis itself is horizontal.

Where a bed is not sufficiently elastic to bend under pressure it breaks, and if, at the same time, the beds on opposite sides of the break slip past each other, faulting is said to occur. When the breaking surface or fault-plane is at a low angle one portion of the bed may be thrust over the other for some distance. In other cases the displacement may amount to but a few inches. Figs. 15 and 16 represent sections in faulted strata, and in these it will be noticed that every bed terminates abruptly at the fault-plane, its continuation on the other side being at a higher or lower level. Displacements of this type are somewhat rare in surface clays, and if occurring, the throw is not apt to exceed a few feet. In the shales of pre-Pleistocene age the amount of displacement is sometimes much greater.

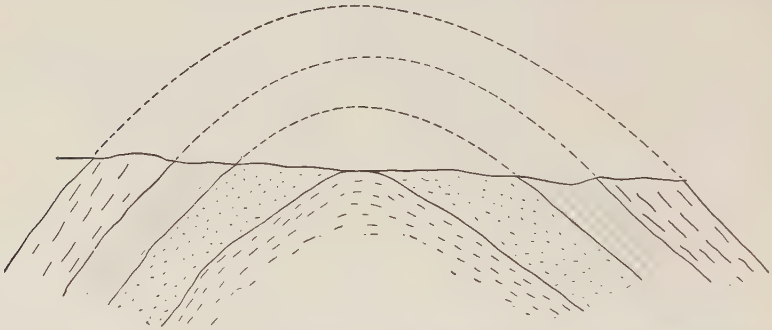

FIG. 14.—Section of folded beds, with crest worn away, exposing different layers. (After Ries, N. J. Geol. Surv., Fin. Rept., VI, p. 18, 1904.)

Both tilting and folding exert an important influence on the form and extent of the outcropping beds. Where no tilting has occurred, that is, where the beds are flat, only one bed, the upper one of the section, will be exposed at the surface, where the latter is level (Fig. 17), and lower beds will be exposed only where stream-valleys have been carved (Fig. 18).

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[1] See Hollick, Trans. N. Y. Acad. Sci., XIV, p. 8, 1894; Clapp, Bull. Geol. Soc. Amer., XVIII, p. 505, 1908; Meinegk sheet, Prussian Geol. Surv., 1906.

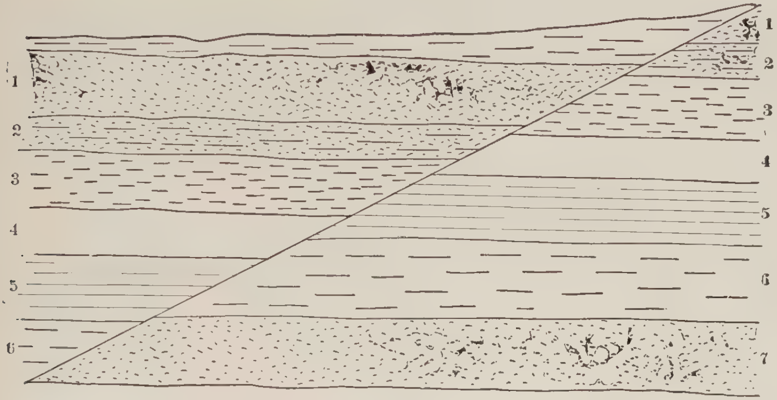

FIG. 15.—Section showing strata broken by fault planes of low inclination. (After Ries, N. J. Geol. Surv., Fin. Rept., VI, p. 15, 1904.)

If the beds are tilted (Figs. 19 and 20) or folded, and the crests of the folds worn off (Fig. 14), then the different beds will outcrop on the surface as parallel bands, whose width of outcrop will decrease with an increase in the amount of dip (Figs. 19 and 20).

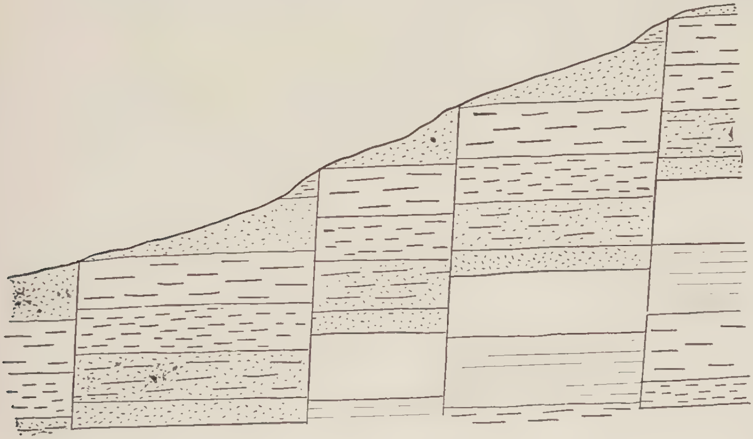

FIG. 16.—Strata broken by parallel fault planes. (After Ries, N. J. Geol. Surv., Fin. Rept., VI., p. 15, 1904.)

Erosion.—All land areas are being constantly attacked by the weathering agents (frost, rain, etc.). The effect of this is to disintegrate the surface rocks and wash away the loose fragments and grains. This brings about a general sculpturing of the surface, forming hills and valleys, the former representing those parts of the rock formations which have not yet been worn away. The effect of this is to cause phenomena or conditions which may at first sight appear puzzling, but are nevertheless quite simple when the cause of them is understood.

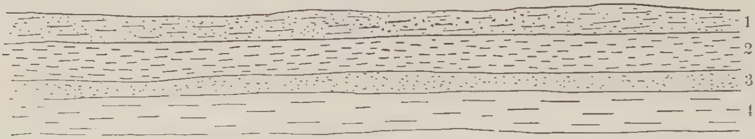

FIG. 17.—Section of horizontal strata with only the top one exposed at the surface.

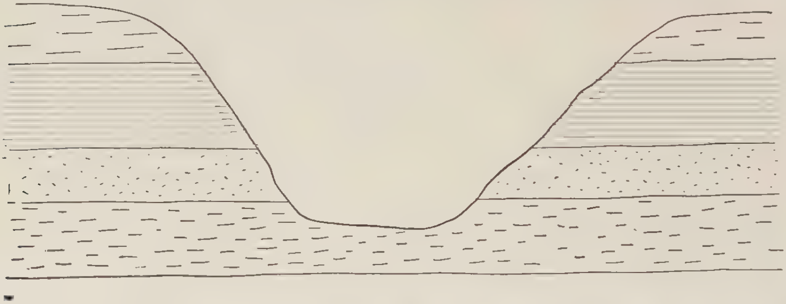

FIG. 18.—Horizontal beds, with several layers exposed by wearing down of the land surface. (After Ries, N. J. Geol. Surv., Fin. Rept., VI., p. 18, 1904.)

Let us take, for example, a section of horizontal clay beds which originally covered an extensive area and were interstratified with sand beds. In Figs. 17 and 21, beds 1 and 3 may be taken to represent the clays. In Fig. 17 we have indicated the surface as it originally was, and in

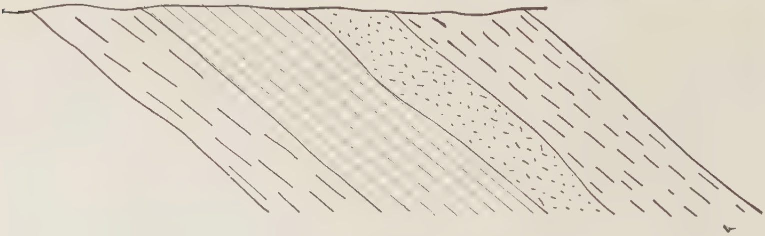

FIG. 19.—Section showing outcropping of tilted beds on a flat surface.

Fig. 21 the outline as it appears after the land has been exposed to weathering and erosion for an extended period. Here we see that the upper bed is left only on the highest hills and has been removed over a large area, while No. 2 caps the smaller knolls, and No. 3 outcrops in the sides of the deeper valleys. Many small areas of clay thus represent all that is left of a formerly extensive bed.

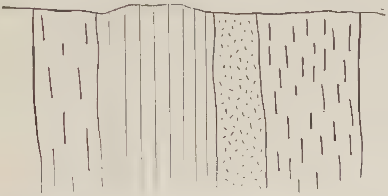

FIG. 20.—Section of vertical beds. The width of outcrop is the same as the actual width of the bed. (See also Fig. 106.)

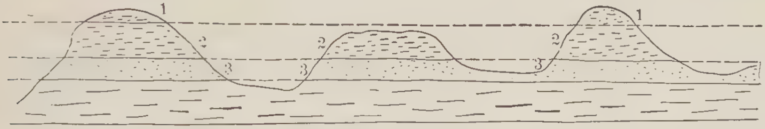

FIG. 21.—Horizontal beds with several layers exposed by erosion of the land surface.

If the beds had a uniform dip, the conditions may be as indicated in Fig. 22. Here bed 1 appears at the summit of two hills, *a* and *b*, but its rise carries it, if extended, above the summit of hill, *c*, which is capped by bed 2. If one did not know that the beds rose in that direction, it might be assumed that bed 1 passed into bed 2, because they are at the same level. This dipping of the layers, or beds, sometimes accounts for the great dissimilarity of beds at the same level in adjoining pits.

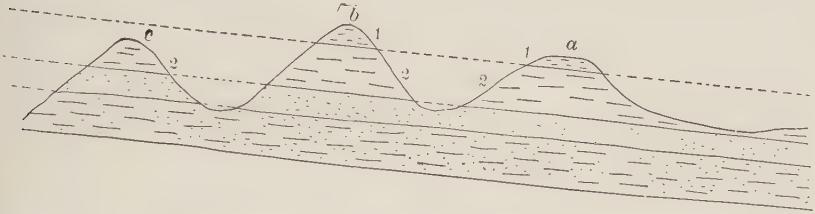

FIG. 22.—Inclined strata showing rise of the beds when followed up the dip. (After Ries, N. J. Geol. Surv., Fin. Rept., VI, p. 19, 1904.)

Where a bed of clay is found outcropping at the same level on two sides of a hill it is reasonable to assume that it probably extends from one side to the other, but it is not safe to predict it with certainty, for, as has been mentioned above, clay beds may thin out within a short distance. Furthermore, the overlying material, or overburden, will become thicker towards the center or summit of the hill, so that even if present the clay may be economically unworkable (Fig. 23).

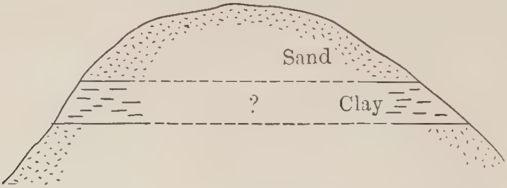

Fig. 23.—Outcrops of a clay bed on two sides of a hill, and probably extension into same. (After Ries, N. J. Geol. Surv., Fin. Rept., VI.)

CHEMICAL CHANGES

Nearly all clay deposits are frequently changed superficially, at least, by the weather or by percolating surface-waters. The changes are chiefly chemical and can be grouped under the following heads:

Change of color.
Leaching.
Softening.
Consolidation.

Change of color.—Most clay outcrops which have been exposed to the weather for some time show various tints of yellow or brown. This coloration, or rather discoloration, is due to the oxidation, or rusting, of the iron oxide which the clay contains. This iron compound is usually found in the clay as an original constituent of some mineral, and rusts out as the result of weathering, so that the depth to which the weathering has penetrated the material can often be told by the color. The lower limit of this is commonly not only irregular, but the distance to which it extends from the surface depends on the character of the deposits, sandy open clays being affected to a greater depth than dense ones. The discoloration of a clay due to weathering does not always originate within the material itself, for in many instances, especially where the clay is open and porous, the water seeping into the clay may bring in the iron oxide from another layer, and distribute it irregularly through the lower clay.

The changes of color noticed in clay are not in every case to be taken as evidence of weathering, for in many instances the difference in color is due to differences in chemical composition. Many clays are colored black at one point by carbonaceous matter, whereas a short distance off the same bed may be white or light gray, due to a smaller quantity of carbonaceous material. In many of the Lower Cretaceous clays of New Jersey, for example, there is often a change from blue to red and white mottled, and from this into red clay. This is not the result of weathering, but is due to local variations in the iron-oxide contents of the different layers.

Discoloration caused by weathering can usually be distinguished from differences in color of a primary character in that the former begins at the surface and works its way into the clay, penetrating to a greater distance along planes of stratification or fissures, and even following plant-roots as shown in Fig. 24.

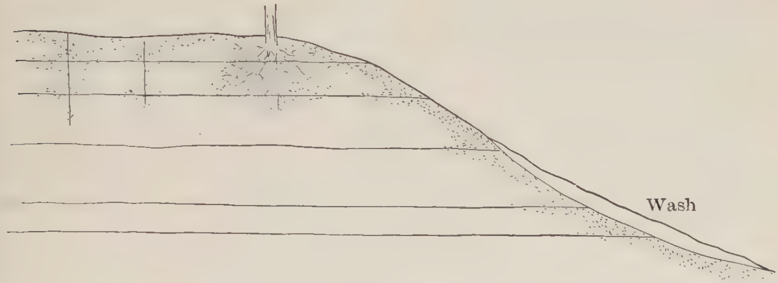

Fig. 24.—Section showing how weathering penetrates a clay bed, particularly along roots, joints and bedding planes.

Where the clay deposit outcrops on the top and side of a hill it does not follow that, because the whole cliff face is discolored, the weather will have penetrated to this level from the surface, but indicates simply that the weathering is working inward from all exposed surfaces. The overburden often plays an important rôle in the weathering of clay, for the greater its thickness the less will the clay under it be affected. This fact is one which the clay-worker probably often overlooks, and therefore does not appreciate the important bearing which it may have on the behavior of his material. Some unweathered clays crack badly in drying or burning, but weathering seems to mellow and loosen them, as well as to increase their plasticity, so that the tendency to crack is sometimes either diminished or destroyed. If a clay which is being worked shows this tendency, it will be advisable to search for some part of the deposit which is weathered, and if the clay is covered by a variable thickness of overburden, the most weathered part will be found usually under the thinnest stripping, as shown in Fig. 25.

Leaching.—More or less surface-water seeps into all clays, and in some cases drains off at lower levels. Such waters contain small quantities of carbonic acid which readily dissolves some minerals, most prominent among them carbonate of lime. In some areas, therefore, where calcareous clays occur, it is not uncommon to find that the upper layers of the deposit contain less lime carbonate than the lower ones, due to this solvent action of the percolating waters, and residual clays from limestone contain little or no lime carbonate.

Waters containing carbonic and organic acids at times leach out the iron from at least the upper portion of a clay deposit.

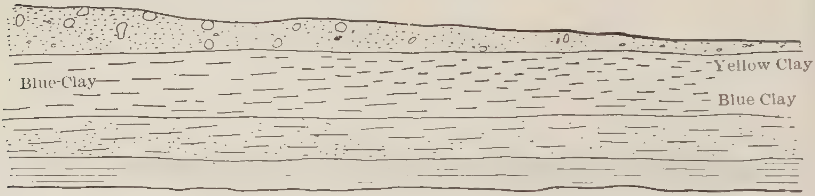

FIG. 25.—Section showing weathered (yellow) clay where the overburden is least.

Softening.—Most weathering processes break up the clay deposits, either by disintegration or by leaching out some soluble constituents that served as a bonding or cementing material, thus mellowing the outcrop, and many manufacturers recognize the beneficial effect which weathering has on their clay. They consequently sometimes spread it on the ground after it is mined and allow it to slake for several months or, in some cases, several years. The effect of this is to disintegrate thoroughly the clay, render it more plastic, and break up many injurious minerals, such as pyrite. Although mentioned under Chemical Changes, it will be seen that the process of softening is partly a physical one.

Consolidation.—This change is found to have taken place in a few deposits, and is due to the formation of limonite crusts in the clay. At times these may form at a few points in the deposit, or only along certain layers, but in other instances they have originated in all parts of the mass, both along the stratification-planes, as well as in every joint or crack. They thus permeate the clay deposit with such a network of rusty, sandstone-like lumps, nodules, and strips as to seriously interfere with the digging of the clay, and requiring powerful machinery to break up the hard parts.

Concretions.—These bodies of foreign matter, often of spherical, lenticular, or rosette-like form, are very abundant in some clays (and shales). They may occur singly, or in rows along the bedding planes. When flattened, the flattening is commonly parallel with the stratification.

Concretions vary in size from small pebbly bodies to occasionally very large ones weighing several hundred pounds (Figs. 27, 28). Among the materials forming them, hydrous iron oxide, siderite and pyrite are not uncommon, the last two sometimes altered in part at least to the first. In many calcareous clays concretions (Fig. 28), consisting largely of lime carbonate are abundant. In others, notably residual ones, chert concretions occur, and these in some instances represent bodies that were present in the parent rock, while in other cases they appear to have formed during weathering. Gypsum, barite, and lime phosphate are also found in concretionary masses.

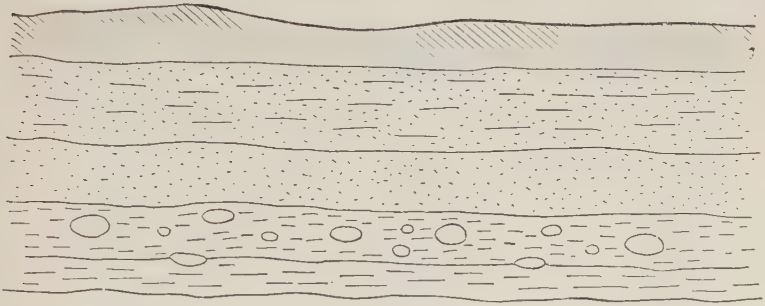

Fig. 26.—Section showing occurrence of concretions in certain layers.

Formation of shale.—Many sedimentary clays, specially those of marine origin, after their formation are covered up by many hundred feet of other sediments, due to continued deposition on a sinking ocean bottom. It will be easily understood that the weight of this great thickness of overlying sediment will tend to consolidate the clay by pressure, converting it into a firm rock-like mass, termed shale. That the cohesion of the particles is due mostly to pressure alone is evidenced by the fact that grinding the shale and mixing it with water will develop as much plasticity as is found in many surface clays. An additional hardening has, however, taken place in many shales, due to the deposition of mineral matter around the grains, as a result of which they become more firmly bound together.

In regions where mountain-making processes have been active and folding of the rocks has taken place, heat and pressure have been developed, and the effect of this has sometimes been to transform or metamorphose the shale into slate or even mica-schist (when the metamorphism is intense), both of which are devoid of any plasticity when ground. The shales utilized for clay products in different parts of the country show a wide variation in their plasticity. Those of the Carboniferous, much used in the Central States, are often highly plastic, while the red shales of the Triassic formation of New Jersey are in most cases consolidated sandy clay, but, with one exception, all those examined are of poor plasticity and very low fusibility. The Hudson River slates, found over a large area of New Jersey, New York, and Pennsylvania, owe their low plasticity partly to a slight metamorphism, and partly to the deposition of cement around the grains.

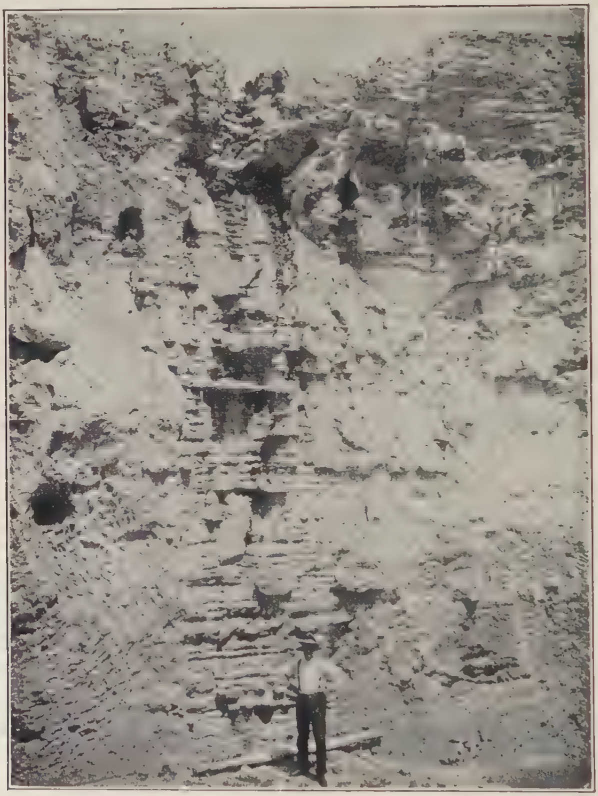

FIG. 27.—Clay bank showing carbonate of iron concretions, Reynolds ore bank, Anne Arundel County, Md. (Md. Geol. Surv., IV, 1902.)

Geologic age cannot be used as a guide towards determining whether the beds of a formation are hard or soft. The Cretaceous of the Atlantic coastal plain contains soft plastic clays, while that of the Rocky Mountain district carries shales which are hard and sometimes flinty in their character.

Some shales which are of no value for clay products in their fresh condition, become workable if they have undergone a relatively slight amount of weathering.

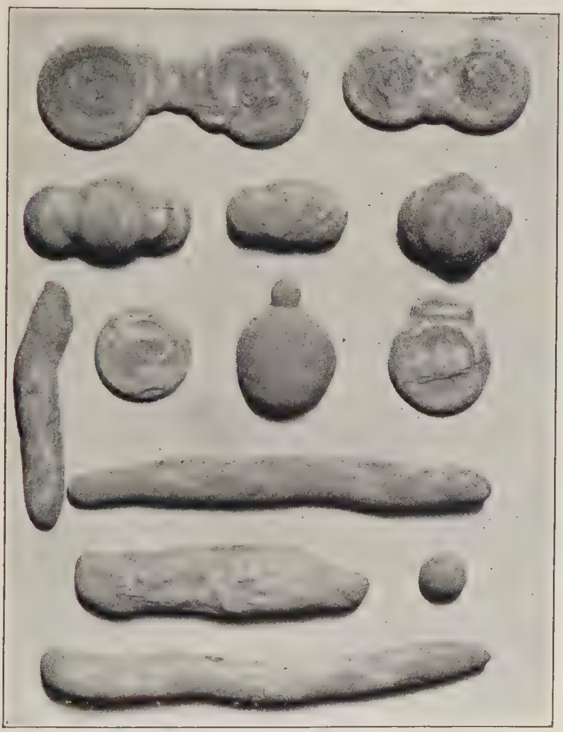

Fig. 28.—Clay concretions (N. J. Geol. Surv., Fin. Rept., VI, 1904.)

Prospecting for Clays

A knowledge of the facts given in Chapter I will, if borne in mind, be of much aid to the clay-worker in prospecting for clays, but several additional points may be mentioned by which beds of clay may be located.

Outcrops.—The presence of a clay-bed is usually detected by means of an outcrop. These exposures are commonly to be found on inclined surfaces, such as hilltops, or where natural or artificial cuts have been made. The washing out of gullies by heavy rains, the cutting of a stream valley, railroad or wagon-road cuts, all form good places in which to look for outcropping clay-beds. The newer the cut the better the exposure, for the sides of such excavations wash down rapidly, and a muddy-red surface-clay or loam will often run down over a bed of lighter colored clay beneath so as to completely hide it from view. If the cut is deep and freshly made the depth of weathering can frequently be determined.

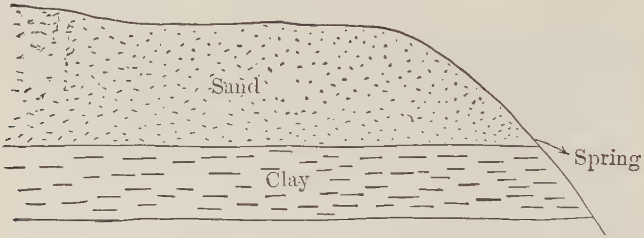

Fig. 29.—Formation of spring due to subsurface water following a clay bed.

Springs.—In many cases the presence of clay is shown by the occurrence of one or more springs issuing from the same level along some hill-slope. These are caused by waters seeping down from the surface (Fig. 29) until they reach the top of some impervious clay stratum, which they then follow to the face of the bank where they issue. The presence of springs, however, cannot be used as a positive indication of clay, for a bed of cemented iron sand, or even dense silt, may produce the same effect (Fig. 30).

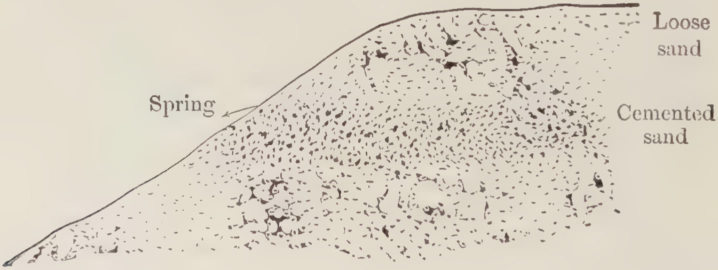

Fig. 30.—Formation of spring due to layer of cemented sand.

Ponds.—In many regions covered by glacial drift, pools of water are often retained in depressions, because of the presence below of a watertight bed of clay (Fig. 31). It does not necessarily indicate a thick deposit, for a very thin layer often holds up a considerable body of water. Such ponds may likewise in rarer instances be caused by ground-water seeping down from higher levels, even in the absence of clay.

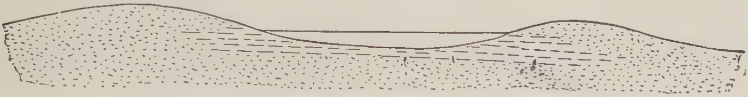

FIG. 31.—Formation of a pond due to a clay-bed beneath a depression.

Vegetation.—Clay-deposits in some areas produce a different type of plant growth from other soils, but the character of the vegetation can only be used as a subordinate aid in the search of clay.

EXPLOITATION OF CLAY-DEPOSITS

The location of a clay-deposit is followed by a determination of its thickness, extent, character, and uses. The first two points and some facts bearing on the third are determined in the field; the behavior of the clay when mixed up and burned is found out by tests made in the laboratory or at some factory, and the information thus obtained indicates the commercial value of the material.

To determine the thickness and extent of the deposit a careful examination should be made of all clay outcrops in neighboring gullies, or other cuts on the property having the clay. Since, however, most clay-slopes wash down easily, it may be necessary to dig ditches from the top to the bottom of the cut or hillside in order to uncover the undisturbed clay-beds. In most cases, however, the cuts are not sufficiently close together and additional means have to be taken to determine the thickness of the deposit at intermediate points. Such data are sometimes obtainable from wells or excavations made for deep cellars, but the information thus obtained has to be taken on hearsay. Borings made with an auger furnish a more satisfactory and rapid means of determining the thickness of the clay-deposit away from the outcrop. A post-hole auger, cutting a hole of three to four inches diameter, can easily be used to a depth of 30 or 40 feet, while one of two inches diameter can be sunk to 100 feet without much difficulty.

From comparison of the data obtained from the bore-holes and outcrops, any vertical or horizontal variations in the deposit can usually be traced. Limonite concretions or crusts, if present in any abundance, are almost sure to be discovered, and even the dryness of the beds can be ascertained. Variations in the thickness of the bed and amount of stripping are also determinable. If small samples are desired for laboratory testing these can be taken from the outcrops and bore-holes, but if large samples are wanted from the intermediate points it is best to sink test-pits where the borings were made.

In some regions the clay-miners make use of an auger to guide them in their digging operations, this being often necessary on account of the rapid variations that may occur in any one deposit.

Baked Clay and Shale

The baking of clay or shale due to the heat produced by burning coal beds has been noted by a number of writers,[1] and some German geologists have called this baked product *Porzellanit* and *Porzellanjaspis* (see Zirkel below).

In places sufficient heat has been generated to bake the shale to a pink, red, purplish red, or even mottled mass, which is hard, and shows a splintery or conchoidal fracture. Some specimens resemble jasper. Occasionally the shale or clay may be more affected locally and develop a vitrified or even slaggy mass. When the last named has cooled slowly, a recrystallization may take place, and various minerals form. Among those which have been identified we find plagioclase, diopside, magnetite, hematite, garnet and sillimanite. Spherulitic structures have also been observed. The coal associated with the baking of the shale is mostly bituminous or subbituminous, and the burning of the latter may be due to spontaneous combustion or oxidation of pyrite, although other causes have been suggested. (Rogers.)

As the burning goes on the overburden slumps down. One case is cited where the burning extended in 500 feet from the outcrop (Bastin) but usually it is never over 200 or 300 feet if the cover is more than 50 or 100 feet and the outcrop fairly straight. (Rogers.) The beds under the coal are not affected.

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[1] Allen, J. A., Proc. Bost. Soc. Nat. Hist., XVI, p. 246; 1874; Bastin, E. S., Jour. Geol., XIII, p. 408, 1905; Collier, A. J., and Smith, C. D., U. S. Geol. Surv. Bull. 341, p. 45, 1909; Dawson, G. M., Rept. on Geol. and Res. of region in vicinity of 49th par., p. 164–169, Montreal, 1875; Hayden, F. V., Geol. Rept. of exploration of the Yellowstone and Missouri Rivers, pp. 56–103, 1869; Hibsch, J. E., Min. Pet. Mitt., XXVII, p. 35, 1908; Leonard, A. G., N. Dak. Geol. Surv., 4th Bien. Rept., p. 79, 1906; Lewis, M., and Clark, W., History of Expedition under the command of Lewis and Clark, I, p. 180, 189, 1814. Phila.; Rogers, G. S., U. S. Geol. Surv., Prof. Pap. 108, p. 1, 1918; Zirkel, Lehrbuch der Petrographie, III, p. 775, 1894.

Two analyses of baked shale are given below.

ANALYSES OF BAKED SHALE FROM FORT UNION FORMATION, MONTANA.

	I	II
SiO_2	65.41	58.30
TiO_2	1.17	.28
Al_2O_3	11.94	20.50
Fe_2O_3	7.38	4.23
FeO	.76	.46
MnO	....	.18
MgO	1.50	1.31
CaO	5.02	4.40
K_2O	1.96	2.28
Na_2O	2.83	1.46
H_2O^-	.08	1.03
H_2O	.50	1.90
CO_2	1.57	3.37
SO_3	.22	.19
P_2O_5	Tr.	Tr.
	100.34	99.89

I. Sandy shale, partly baked, Upper Tongue River, T. 9 S., R. 40 E. The slag showed diopside and plagioclase.

II. Clay shale, T. 1N., R. 36 E. Moderately baked. The slag from this showed sillimanite, cordierite and probably spinel. (G. S. Rogers, Analyst.)

CHAPTER II

MINERALS IN CLAY

Introductory.—The complex mineralogical character of clay has been referred to on an earlier page, and a microscopic examination or chemical analysis of a few impure clays will convince one of this fact.

Nevertheless the statement is often made in print that clay is a hydrated silicate of alumina having the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, consequently of definite chemical composition and with a formula corresponding to that of the mineral kaolinite.

That this explanation is clearly improbable can be seen by examining any series of clay analyses, few of which will reduce to such a formula.

Equally sweeping and incorrect is the statement that kaolinite is the basis of *all* clays, and that they are therefore to be regarded as a mixture of kaolinite with other minerals.

Many clays no doubt contain a variable amount of kaolinite,[1] but there are others, consisting almost entirely of silica, alumina, and water, which clearly do not correspond to the formula of the mineral above mentioned (see Halloysite), and in impure clays it becomes a matter of some difficulty to prove beyond a doubt whether the hydrous aluminum silicate present is kaolinite or some other mineral.[2] We may even express reasonable doubt regarding the necessary presence of kaolinite for the development of plastic qualities in the mass.

Microscopic examination.—The identification of minerals in clay is not without difficulty for the obvious reason that the grains are so small and must often be studied with the highest powers of the microscope. Even so there are many extremely minute particles whose identification, with certainty at least, is practically impossible. There is moreover a variable amount of colloidal matter. (See Colloids under Plasticity.)

The petrographic work which has been done on clay, consists in part of investigations of a general character, of which a number have been published, and in part of special investigations. References to a number of the former are given below,[1] while the latter are mostly referred to under the special minerals to which they relate.

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[1] Kaolins of commerce and ball clays.

[2] This fact has also been emphasized by G. P. Merrill, Non-metallic Minerals, p. 217, 1904.

While the microscopic examination of clays has usually been made on the powdered material using either the petrographic microscope or index liquids,[2] a method more recently employed has been to soak the clay in some hardening medium and then section it.[3]

Preparation of thin sections.—The method consists in placing a chip of the material to be sectioned on a hot electric plate, with a fragment of hard kollolith on top of it; or the fragment can be placed face downward in a small metal dish containing kollolith. "The capillary force will cause the melted kollolith to penetrate throughout the specimen if the pores are large. The whole operation will not take over 15 minutes and grinding may be begun as soon as the chip is cooled." "It is best to maintain a temperature of 150° to 170° for impregnating porous materials with melted kollolith."

"Fine-grained compact materials may not absorb the melted kollolith which is rather viscous, and then a solvent must be used to thin it and carry it into the minute pores of the rock. For this purpose the kollolith dissolved in xylol that comes ready prepared may be used, or the hard kollolith may be used and a little fresh xylol added." "The xylol-kollolith solution may be applied directly to the upper surface of the heated chip or it may be placed in a metal dish containing the solution." The specimens are heated for an hour or more to drive off the excess xylol.

Since shales and clays contain minerals that soften or swell on contact with water, no water can be used in the grinding.

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[1] G. Hickling, The Microscopic character of China clay, Jour. Soc. Dyers and Colorists, XXXI, p. 70, 1915; W. J. McCaughey, The Mineralogical Examination of Clays, Trans. Amer. Ceram. Soc., XV, p. 322, 1913; H. G. Schurecht, The Microscopic Examination of the Mineral constituents of some American Clays, Jour. Amer. Ceram. Soc., V, p. 3, 1922; Anon., Blue and Black Ball Clays under the microscope, Pot. Gaz., XLII, p. 892, 1917; Bertrand, L. and Lanquine, A., Cer., XXV, p. 97, 1922, also Compt. rend., CLXIX, p. 1171–4, 1919; Bertrand, L., The use of the Petrographic Microscope in Ceramics to examine the structure of clay in the raw and fired state, Ceramique, XXVI, p. 180–94, 1923; Bertrand, L., Micrographic examination of the Structure of Clays, Récherces et inventions, IV, p. 825–33, 841–51, 1923; Coon, J. M., Chem. Age (London), VIII, No. 209, China Clay, Trade Review, Sec. 8, 15, 1923; McCaughey, W. J., and Fry, W. H., U. S. Bur. Soils, Bull. 91; McCaughey, W. J., Mineralogical Soil Analysis, Jour. Ind. Eng., Chem., V, p. 562; Ross and Shannon, Jour. Amer. Ceram. Soc., IX, p. 77, 1926; Fry, W. H., Econ. Geol., X, p. 292, 1915; Cayeux, L., Roches Sédimentaires, 1916.

[2] Staining may also yield information. See Steinhoff, E., and Hartman, F., Stahl u. Eisen, XLV, p. 337, 1925.

[3] Ross, C. S., Econ. Geol., XXI, p. 454, 1926.

The rough grinding is done on emery or carborundum paper. The final grinding is done with oil on a carborundum hone, or the flat side of a fine-grained carborundum wheel. The liquid for hand grinding is a mineral medicinal oil such as nujol.

Ultramicroscope.—A second possible line of attack is with the ultramicroscope, and is one which offers interesting possibilities, but which has been little tried.

Some interesting results in this field have been obtained by Alexander,[1] who studied a series of high grade clays, and estimated the relative amount and size of colloidal particles present, the latter property being based on the brightness of their diffraction images and the nature of their motion.

He points out that the motion of some colloidal particles is *hampered,* meaning that they acted as though some crystalloid salt or other coagulant was present. This the author terms *crystalloidisis.*

Dehydration curve.—A third possible line of study, is by use of a heating curve,[2] it being well known that if clay or hydrous aluminum silicates are heated through a range of temperature from 100°–1000° C., that the loss curve instead of being straight, may show a terrace at those points where endothermic reactions occur, and humps to indicate exothermic reactions.

This method of examination is interesting, but is of restricted value unless one can be sure that the material examined is pure.

X-Ray examination.—Finally the study of clays with the X-ray apparatus, shows promise of becoming important.[3]

Minerals recorded.—The number of different minerals present in a clay is often no doubt large and depends partly on the mineralogical composition of the rock or rocks from which the clay has been derived, and partly on the extent to which the mineral grains in the clay have been destroyed by weathering; but in any case the identification of mineral species is rendered rather difficult, chiefly because of the extreme fineness of the grains, and partly because these are often surrounded by decomposition products.

More attention has been given to the mineralogy of soils than of clays, but since the former are in many cases nothing more than surface clays, what is true of the one is more or less so of the other.

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[1] Jour. Amer. Ceram. Soc., III, p. 621, 1920; see also Fry, W. H., The Microscopic Estimation of Colloids in Soil Separates, Jour. Agric. Research, XXIV, 879, 1923.

[2] See Mellor, J. W., Trans. Ceram. Soc. (Eng.), XVI, p. 72, 1917. See also under Dehydration.

[3] See Hadding, A., Trans. Ceram. Soc. (Eng.), XXIV, p. 27, 1925; Navias, L., and Davey, W. P., Jour. Amer. Ceram. Soc., VIII, p. 640, 1925; Schwartz, R., Keram. Rund., XXXII, p. 538, 1924; Jour. Soc. Glass. Tech., VIII, p. 298.

Chamberlin and Salisbury,[1] in studying the residuals of the Wisconsin driftless area, were able to identify such minerals as plagioclase, orthoclase, biotite, muscovite, hornblende, augite, magnetite, and quartz, while Ladd, in studying the Georgia Cretaceous clays,[2] has noted kaolinite, feldspar, quartz, muscovite, biotite, magnetite, titanite, limonite, calcite, and prochlorite. In the Wisconsin materials Buckley [3] records finding quartz, feldspar, mica, calcite, dolomite, and iron oxide. The Leda clays of Canada [4] show quartz, orthoclase, plagioclase, mica, tourmaline, pyroxene, chlorite, and hornblende.

In the study of soils perhaps the largest number of species have been determined by Delage and Lagatu,[5] who include in their list calcite, quartz, biotite, muscovite, sericite, orthoclase, oligoclase, zircon, tourmaline, amphibole, apatite, andalusite, titanite, microcline, limonite, hematite, chlorite, augite, etc.

The work of R. E. Somers on a series of high-grade clays [6] has brought out the interesting fact that hydromica is widely distributed in them, and in many cases is as abundant or more so than the recognizable kaolinite. Four other widely distributed minerals are quartz, rutile, zircon and tourmaline.

A number of hydrous aluminum silicates, which some term the "clay minerals," have been described, but it may be questioned whether they are all valid species.

Ross and Shannon [7] state "that the study of bentonite and some other related clays seem to indicate that the clay minerals are few in number and that each is a single definite chemical compound of simple type rather than an isomorphous mixture of two or more dissimilar end members." Pure clays, which they studied, were composed of one of the following five distinct clay minerals, two of which have been found in bentonite and the other three in non-bentonitic clays. The five are: Montmorillonite, beidellite, micaceous halloysite, amorphous halloysite, and kaolinite. It will be interesting to see if this statement holds true.

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[1] U. S. Geol. Surv., 6th Ann. Rept., 245.

[2] Amer. Geol., XXIII, p. 240, 1899.

[3] Wis. Geol. and Nat. Hist. Surv., Bull. VII, Pt. I.

[4] Merrill, Rocks, Rock-weathering, and Soils, p. 335.

[5] Ann. de l'école nationale d'agriculture de Montpellier, VI, pp. 200–220, 1905; also Comptes rend., CXXXIX, p. 1044, 1904. See also F. Steinriede, Anleitung zur mineralogischen Bodenanalyse, Halle, 1889; Dumont, Compt. rend., CXL, p. 1111, 1905; Tebier, *ibid.*, CVIII, p. 1071, 1889; and Cameron and Bell, Bur. of Soils, Bull. 30, p. 11, 1905, and Bull. 22, p. 12, 1903.

[6] U. S. Geol. Surv., Bull. 708, p. 292, 1922, also Jour. Wash. Acad. Sci., IX, 1919.

[7] Jour. Amer. Ceram. Soc., IX, p. 87, 1926.

H. Stremme[1] has published a long series of articles on the clay minerals, but the results are based on chemical instead of petrographic work.

HYDROUS ALUMINUM SILICATES

Kaolinite.—This mineral is a hydrated silicate of alumina, represented by the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, which corresponds to a composition of Silica (SiO_2), 46.3 per cent; Alumina (Al_2O_3), 39.8 per cent; Water (H_2O), 13.9 per cent. It is a white, pearly mineral, crystallizing in the monoclinic system, the crystals presenting the form of small hexagonal plates (Fig. 32) with a hardness of 2–2.5 and a specific gravity of 2.2–2.6. It is naturally white in color, and a mass of it is plastic when wet, but very slightly so.

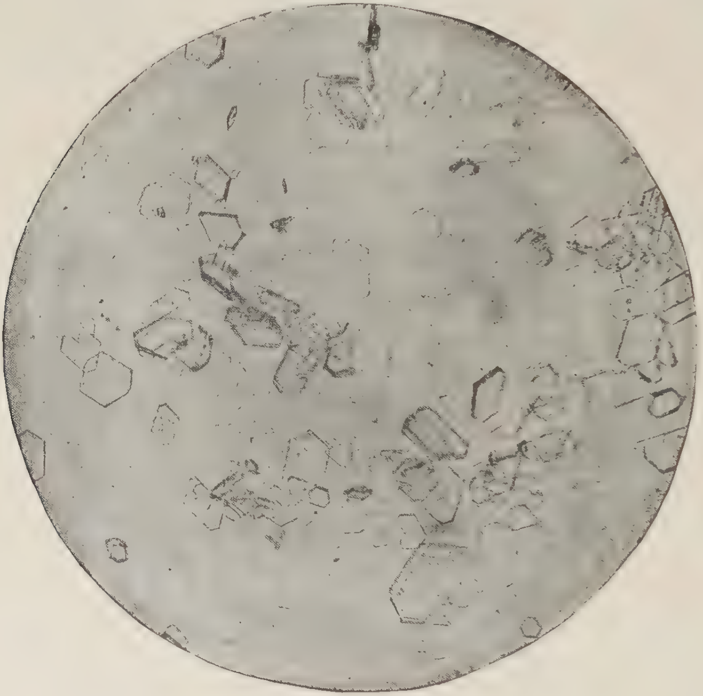

FIG. 32.—Photo-micrograph of kaolinite. (After Merrill, Non-metallic Minerals.)

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[1] Sprechsaal, XLVII, pp. 145–7, 163–6, 181–3, 201–3, 215–8, 233–5, 251–3, 269–70, 283–5, 302–4.

The name kaolinite was suggested by S. W. Johnson and J. M. Blake,[1] who expressed the opinion that minerals variously named as pholerite, nacrite, steinmark and kaolin really belong to one mineral species with definite chemical and physical properties. They proposed the name kaolinite because "kaolin furnishes it most commonly and abundantly."

It has naturally been assumed by most writers that kaolinite was a widely distributed mineral in clays, but when we come to sift the evidence of its presence comparatively little is to be found.

A microscopic examination even of the white clays free from impurities rarely reveals the presence of the hexagonal kaolinite scales, although the little vermiculite-like bunches of plates of this mineral may be present (Fig. 33); but still even these are rarely seen in the more impure clays, and the theory of the universal presence of kaolinite in clay is probably traceable to the fact that many white clays, after having the sand washed out, often approach kaolinite in composition.[2]

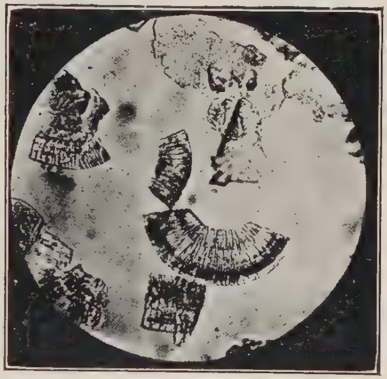

FIG. 33.—Photo-micrograph of particles of washed kaolin. (After Rieke, Sprechsaal, XL, p. 33, 1907.)

Many kaolins show the bunches of kaolinite plates referred to above, and the separation of these by grinding was said by Cook [3] to increase the plasticity.

Staining appears in some cases to have more clearly shown the structure of the kaolinite plates, for Rieke,[4] in describing some crystalline kaolinite from Hirschau, Bavaria, showed that the crystals stained with methylene blue, are lamellar and exhibit a zonal structure parallel to the edges. Very thin flakes were also found as well as fragments of spherical particles. The former showed distinctly a porous structure, and analysis proved them to be practically identical with kaolinite.

As pointed out by Galpin,[5] the fans frequently show ribs or plates of higher index and birefringence intergrown with those of kaolinite, and he adds that "these ribs show practically every grade of variation between kaolinite and muscovite."

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[1] On Kaolinite and Pholerite, Amer. Jour. Sci. (2), XLIII, p. 351–361 and 405–406.

[2] H. Ries, Ala. Geol. Survey, Bull. 6, p. 41, 1900.

[3] Clays of New Jersey, N. J. Geol. Surv., 1878.

[4] Sprechsaal, XL, p. 33.

[5] Trans. Amer. Ceram. Soc., XIV, p. 307, 1912.

A similar condition had been previously described by Hickling,[1] as a result of which he argued that muscovite represents a transition stage in the weathering of feldspar to kaolinite. Selle[2] has noted the same thing. Somers[3] observed the occurrence of good "fans" in clays from Perry, Ga., Bynum, Ala., and Bauxite, Ark., while good examples of vermiculites were seen in some of the white Cretaceous clays of Georgia and South Carolina. C. E. Miller has noted a great abundance of fans of kaolinite in sandy residues from washed North Carolina kaolins.[4]

These fan-shaped bundles have however been noted by a number of other observers.[5]

The white clays from Edgar, Fla., and Langley and Aiken, S. Carolina, exhibit large single flakes of kaolinite.

Optical and crystallographic properties.—Crystals of kaolinite are rather rare. They have been noted by H. Reusch from the National Belle Mine, Red Mountain, Colo.,[6] by A. B. Dick from Anglesey,[7] as well as by several others.[8]

The optical properties of kaolinite have been given by several different investigators.

Reusch,[9] reported the crystals from Colorado to be (orthorhombic).

A. B. Dick[10] regarded the kaolinite from Anglesey as monoclinic, and Miers[11] after examining the material confirmed this view. The optical properties given by them are: axial angle $\beta = 83° 11'$, $a : b : c =$

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[1] Trans. Inst. Min. Engrs. (Eng.), XXXVI, p. 10, 1908–9.

[2] Chem. Centralb., 1908, XI, 1903.

[3] U. S. Geol. Survey, Bull. 708, p. 296, 1921.

[4] Personal communication.

[5] Johnson and Blake, A. J. S., ii, XLII, pp. 351 to 361, and 405–406; Merrill, Non-metallic Minerals; Reusch, Neues Jahrb. Min., 1887, II, p. 70; Rieke, Sprechsaal, XL, p. 34, 1907; Cook, N. J. Geol. Surv., Clays, 1878, p. 280; Mellor, Trans. Eng. Ceram. Soc., VIII, 1908–9; Ries, Md. Geol. Surv., IV, Pt. III, p. 250, 1902.

[6] Neues Jahrb. Min., 1887, II, p. 70; also L. Milch, Centralbl. Min. Geol., 1908, 1–3.

[7] Min. Mag., 1876, VIII, p. 15.

[8] Safarik, Böhm, Ges. Wiss., 16th Feb., 1870; Knap, Neues Jahrb. Min., etc. 1859, p. 595; Johnson and Blake, Amer. Jour. Sci., ii, XLII, pp. 351 and 867; Ehrenberg, Pogg. Annal, XXXIX, p. 104; v. Fritsch, Tonind. Zeit., 1881, p. 371; Butler, Min. Mag., XVI, No. 73; Schaller and Bailey, Jour. Wash. Acad. Sci., VI, p. 67–68, 1916.

[9] Neues Jahrb. Min., 1887, Bd., II, p. 70.

[10] Min. Mag., VIII, 1888 (1889).

[11] Min. Mag., XV, p. 124, 1908.

.5748 : 1 : 5997. Dick gives the mean refractive index for sodium light as 1.563, and found the Anglesey material to be positive. $2V =$ about 68°. Dispersion feeble. On biaxial plane, $\gamma - \beta = .004$; on plane of symmetry, $\beta - \alpha = .002$.

He expressed the opinion that the statement in many books that kaolinite is negative appears to be based on A. Des Cloizeaux's [1] examination of varieties of pholerite and nacrite, when he observed through the basal cleavages, a wide-angled negative bisectrix.

Dick reports that a nacrite from Freiberg, Saxony, had the same composition, hardness, gravity, and index as the Anglesey material, but was optically negative with the acute bisectrix practically normal to the cleavage and $2E = 103°$ approximately, hence $2V = 60°$. He concluded that there were two varieties of kaolinite, a positive and a negative, the former more common and better crystallized.

E. Kaiser [2] gives the refractive index of kaolinite as between 1.551 and 1.559 with a double refraction of .005–.006.

Larsen [3] gives the properties as: Biaxial, positive. $\alpha = 1.561$; $\beta = 1.563$; $\gamma = 1.567$. $2V$ large; $\rho < v$ perceptible; $Z = b$, $Y \wedge a = 11°$.

The low index of refraction and low birefringence help to distinguish it from other micaceous minerals.

Formula of kaolinite.[4]—The two following analyses represent the composition of pretty pure kaolinite from I, Anglesey, and II, Red Mountain, Colorado.

	I	II
SiO_2	46.53	46.35
Al_2O_3	38.93	39.59
H_2O	13.87	13.93

These analyses correspond closely to the formula,

$H_4Al_2Si_2O_9$, or SiO_2, 46.5; Al_2O_3, 39.5; H_2O, 14 per cent.

The chemical constitution of the kaolinite molecule, has been variously written by different writers, the results being summarized as follows:

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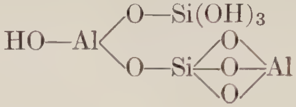
[1] Manuel de Mineralogie, 1862, Vol. I, p. 190, 549.

[2] Neues Jahrb., 1907, Bd. II, p. 42–64.

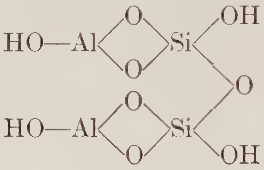
[3] Personal communication, March, 1927.

[4] Mellor and Holdcroft, Trans. Ceram. Soc. (Eng.), X, p. 94, 1911, and XI, p. 169, 1912. Also J. A. Howe, Handbook to collection of Kaolin, etc., Museum Prac. Geology, London, 1914.

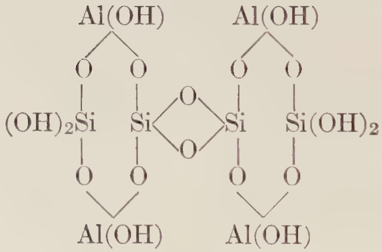
F. W. Clarke and H. C. McNeil.


(1)

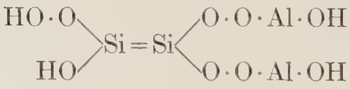
K. Haushofer, also F. Hundeshagen and W. Pukall.


(2)

V. I. Vernadski.


(3)

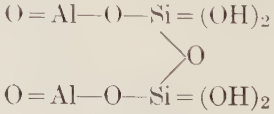
C. Simmonds.


(4)

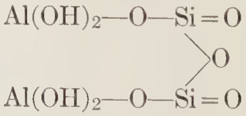
R. Brauns.

$2(Al_2O_3 \cdot SiO_2 \cdot 3H_2O)Al_2O_3 \cdot 3SiO_2.$ (5)

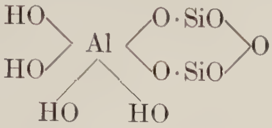
P. Groth.


(6)

R. Scharizer.

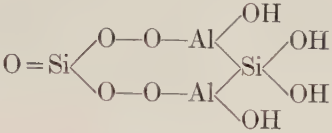

(7)

J. W. Mellor and A. D. Holdcroft.



(8)

Y. V. Samoilov.



(9)

Effect of heat on kaolinite.—Kaolinite loses water and becomes more soluble in acids on heating to redness, but heating to a white heat makes it resistant to acids.

C. W. Kanolt gives the melting point of kaolin as 1740° C.[1]

Dehydration.—It is somewhat difficult to obtain a sufficiently large quantity of pure kaolinite for testing, and so most of the recorded tests have been made on samples of kaolin (usually washed) which closely approached kaolinite in composition.

The following tests are given by E. A. Wülfing.[2]

Dehydration Tests of Kaolinite. (Wülfing)

Loss of weight	Kaolinite			Steinmark from Rochlitz
	Znaym	China	Passau	
To 108° C.	.43	.47	1.30	.85
108°–250°	.22	.21	1.01	.28
250°–350°	.24	.27	.85	.34
350°–500°	9.75	11.19	9.92	12.07
Over 500° C.	1.97	1.70	1.74	1.59
108°–Red heat	12.18	13.37	13.52	14.28

J. W. Mellor and A. D. Holdcroft,[3] concluded from figures given below that there is no definite temperature of dehydration of either china-clay or kaolinite crystals.

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[1] U. S. Bur. Stand. Technol. Paper, No. 10, 1912.

[2] Jahresb. Ver. vaterl. Naturk. Württ., 1900, I; quoted in Doelter's Handbuch der Mineralchemie, 2, II, p. 83.

[3] Trans. Ceram. Soc. (Eng.), XI, p. 169, 1911–12.

Loss on ignition of china-clay and kaolinite crystals when heated for one hour at different temperatures are shown below:

Dehydration Tests of China-clay and Kaolinite.
(Mellor and Holdcroft)

Temperature	China-clay		Butler's Kaolinite	
	Vacuum	Atmospheric Pressure	Vacuum	Atmospheric Pressure
300° C.	.24	.26	1.66	1.82
400	.89	.57	1.70	1.91
425	1.43	.68	1.80	
450	3.38	.80	2.72	
500	8.48	1.19	4.96	2.41
550	....	....	8.20	6.00
600	....	11.92	11.58	10.88
Loss on ign.	12.64		15.94	

According to S. Satoh,[1] who made a study of the heating and cooling curves of Japanese kaolinite, this showed changes at about 600° C. and at 900°–1000° C. where it became isotropic, granular at 1250°–1300° C., and developed "sillimanite" near 1400° C. Satoh points out an endothermal reaction from 450° to 700° C., an exothermic near 950°, and another one at 1200° to 1300° C. The differential heating and cooling curves were plotted with quartz sand as a comparison substance, on which account they have been criticized by E. W. Washburn, because of Satoh's neglect to consider the endothermal change of quartz from the α to the β form at 575° C.

An exothermic change was noted by LeChatelier about 925°, and also by Ashley,[2] while Mellor and Holdcroft [3] placed it at about 900° C.

The last named authors also concluded from their experiments that above 500° kaolinite dissociates into free alumina, free silica and water, the exothermic change noted by them at 900° being possibly a physical change in the alumina.

Sokoloff,[4] agreed with Mellor and Holdcroft, his conclusions being based on solubility in hydrochloric acid of clays heated to various temperatures.

[1] Jour. Amer. Ceram. Soc., IV, p. 182, 1921.

[2] Jour. Ind. Eng. Chem., III, p. 91–5, 1910.

[3] Trans. Ceram. Soc. (Eng.), X, p. 94–120.

[4] Tonind. Zeit., XXXVI, p. 1107–1111.

Various authors have commented on the loss of combined water within a certain temperature range, and have recorded different endothermic ranges.

Brown and Montgomery[1] state that the bulk of the water is driven off at 450° C., the action being slow at first but becoming rapid at 500°, and the final portion passing off at a temperature of not less than 800° C.[2]

Effect of heat on optical properties of kaolinite.—According to A. A. Klein[3] kaolinitic material becomes isotropic when heated to 600° C., with but a slight change in the index of refraction, and there was no marked change in the optical properties until 1200° C. was reached. At this point dissociation of the kaolinitic material resulted in formation of two isotropic substances one of which was: $n = <1.50$ and the other, $n = >1.60$.

Complete dissociation occurred at 1400° C. Between 1400° and 1450° nearly all the minute isotropic higher refracting grains assumed a prismatic development, and some were found to be biaxial and positive, with the plane of the optic axis parallel to the prism axis, agreeing according to Klein with the properties of sillimanite, $Al_2O_3 \cdot SiO_2$.

Rieke says that only a few grains of the clay are crystalline and most are amorphous, but have nevertheless been closely studied and seem often to have a definite chemical composition[4] and not as some consider them, merely mixtures of alumina and silica gels.[5]

Effect of heating on solubility of kaolinite.—Clarke[6] states that after dehydration at low redness, kaolin is completely decomposed by hydrochloric acid, but the ignited mass contains no silica soluble in sodium-carbonate solution. These facts he thinks indicate the formation of a salt $Al_2Si_2O_7$ as a result of ignition, but other interpretations he considers possible.

Mellor[7] says it is wrongly taken for granted on the authority of LaCroix[8] that kaolinite is not attacked by HCl, but that P. Berthier[9] and quoted by Mellor and Holdcroft[1] had stated in 1847 that concentrated boiling HCl easily attacks it partially. Mellor thinks the diverse statements due to the fact that the crystalline form of kaolinite is more slowly broken down than the colloidal form.

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[1] U. S. Bur. Stand. Tech. Paper No. 21, 1913.

[2] See also P. A. Granger, La Céramique industrielle, 1905, p. 5; L. Lefevre, Les Industries céramiques, Fasc. I, 1906, p. 17–18; A. Heath and J. W. Mellor, Trans. Ceram. Soc. (Eng.), VII, p. 80–100; Doelter, Handbuch der Mineralchemie, II, p. 82, 1917.

[3] U. S. Bur. Stand. Tech. Pap. 80, pp. 11 and 35, 1915; and Trans. Amer. Ceram. Soc., XVIII, p. 377, 1916.

[4] M. J. Thugutt, Zenntralb. Min. Geol. and Pal., 1911, No. 4, p. 97–103.

[5] Stremme, *ibid.*, 1908, p. 622.

[6] U. S. Geol. Surv., Bull. 588, p. 40.

[7] Trans. Ceram. Soc. (Eng.), XVI, Pt. I, p. 80.

[8] Soc. Min. de la France, I, p. 472, 1895.

[9] Traité essais Par la voie sêche. Liège. I, p. 68. 1847.

Howe[2] states that kaolinite is very slightly attacked by hydrochloric acid, and decomposed by concentrated boiling sulphuric acid.

Varieties.—Mellor[3] has expressed the opinion that there are three definite minerals corresponding with the empirical formula $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$, viz.: Kaolinite (positive) and nacrite (negative) which are crystalline, and clayite (see below) which he believes is a colloidal form.

He does not regard clayite and amorphous halloysite as identical. According to him kaolinite, clayite and halloysite are easily differentiated by their time temperature curves as follows:

Terrace at 900° C.	Terrace at 500° C.	No terrace at 150° C. Kaolinite
	No terrace at 500° C.	Terrace at 150° C. Clayite
		Terrace at 150° C. Halloysite

His further belief is that the hydrous aluminum silicate minerals, halloysite, allophane, severite, montmorillonite, razoumoffskite, lenzinite, cimolite, confolensite, collyrite, anauxite, smectite, and indianaite are probably mixtures of gels of colloidal silica and alumina hydrates. This sweeping statement can hardly be considered correct in the light of our present knowledge.

A peculiar kaolinite, which intumesces strongly on heating has been described from Back Bone Mountain, LeFlore County, Okla.[4] Its analysis was: SiO_2, 46.55; Al_2O_3, 38.90; H_2O, 14.04. The microscope showed it to be composed of small hexagonal plates, whose refractive indices were, α, 1.561; β, 1.563; γ, 1.567.

Origin of kaolinite.—From what has been said regarding the origin of residual clays and in particular kaolin (p. 3), there would seem to be little doubt that it is a secondary mineral, whether formed by ascending or descending waters, and that in the majority of cases it is formed under low temperature conditions.

Feldspar appears to be the common parent mineral, although it appears quite possible that sericite may sometimes at least be an intermediate product.

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[1] Trans. Ceram. Soc. (Eng.), IX, p. 94, 1911.

[2] l.c., p. 146.

[3] Trans. Ceram. Soc. (Eng.), XVI, Pt. I, p. 83, 1917.

[4] Schaller, W. T., and Bailey, R. K., Jour. Wash. Acad. Sci., VI, pp. 67–68, 1916.

Some writers however express the opinion that it may be derived from a number of other minerals, and while it is possible in many cases to write a chemical equation showing such a change, other evidence is often lacking.

Thus Rösler[1] states that the formation of kaolinite from scapolite, leucite, nepheline, sodalite, hauyne, analcite, topaz, etc., is chemically possible, but not proven.

The same may be said in part regarding the statements of Van Hise,[2] who lists andalusite, anorthoclase, biotite, cyanite, epidote, leucite, microcline, nephelite, orthoclase, plagioclase, scapolite, sillimanite, sodalite, topaz, zoisite, and garnet as the primary mineral. He gives the formula for the kaolinization of feldspar as follows:

$$2KAlSi_3O_8 + 2H_2O + CO_2 = H_4Al_2Si_2O_9 + 4SiO_2 + K_2CO_3.$$

Van Hise calculates that the decrease in volume, supposing the freed silica as quartz, and the potassium carbonate dissolved, is 12.57 per cent. If all the silica were dissolved (which is unlikely), then the volume decrease would be 54.44 per cent.

MINERALS RELATED TO KAOLINITE

These include several species, all hydrated silicates of alumina. Some of these have been found in crystals and are very probably good species, but others are known only in an amorphous condition, which may tend to suggest some doubt as to their validity; in fact Johnson and Blake[3] suggested that the name *kaolinite* should include all the associated species mentioned below, and that the term *kaolin* be retained for the "more or less impure commercial article," but this usage seems too comprehensive, especially since some of those hydrous aluminum silicates mentioned below seem to have a definite formula distinctly different from that of kaolinite proper. These associated species together with their characters are given by Dana and others as follows:

Halloysite.—This name was first applied by Berthier,[4] to a white mineral found in the Carboniferous limestone at Angleur near Liège, Belgium. Breithaupt later applied the names Galapektite and Gummite to a heavy creamy and light gum-like variety.[5]

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[1] l.c. See also Fiebelkorn, Baumaterialienkunde, IV, p. 280.

[2] Treatise on Metamorphism, p. 352.

[3] Amer. Jour. Sci., ii, XLII, p. 351.

[4] Ann. Ch. Phys., XXXII, p. 332, 1826.

[5] Howe, J. A., Handbook to Collection of Kaolin, etc., Mus. Prac. Geol., London, 1914.

The material called halloysite occurs usually as a massive, claylike or earthy material with a conchoidal fracture and often resembles unglazed porcelain. Its other properties are: isotropic; *n*, 1.470–1.542 (Larsen); cleavage, none; hardness, 1–2; specific gravity, 2–2.2; luster pearly to waxy or dull; color white, grayish, greenish, yellowish and reddish; insoluble in acid; infusible. On long exposure to dry air, or on heating to 60° C. for a few hours the index increases to 1.555.

It is a hydrous silicate of alumina like kaolinite, but apparently either crystalline or amorphous and containing more water; the amount is somewhat uncertain, but according to LeChatelier, the composition is probably $2H_2O, Al_2O_3, 2SiO_2 + aq$, or SiO_2, 43.5 per cent; Al_2O_3, 36.9 per cent; H_2O, 19.6 per cent = 100. Some regard it as an amorphous kaolinite.

A. F. Rogers[1] gives the index as ranging from 1.538–1.557, and expresses the opinion that its use is probably a safer means of distinguishing halloysite from kaolinite than the absence of double refraction.

A number of occurrences of the material have been described by different authors.

It is not uncommon in the kaolin deposits around Valleyhead, DeKalb County, Ala.,[2] where it occurs as veins in the kaolin, but no analysis of the material is available.

A deposit has been described by Wheeler[3] from five miles southwest of Aurora, Mo. The material is a white porcelain-like clay, which is more or less stained or intermixed with yellow clay. It is massive, compact, hard, and of low plasticity. It fuses completely at 2600° F. and has the following composition:

ANALYSIS OF MISSOURI HALLOYSITE

Silica (SiO_2)	44.12
Alumina (Al_2O_3)	37.02
Ferric oxide (Fe_2O_3)	.33
Lime (CaO)	.19
Alkalies (Na_2O, K_2O)	.24
Water (H_2O)	18.48
Total	100.38

This analysis it will be seen agrees closely with the theoretic composition of this mineral given above.

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[1] Jour. Geol., XXV, p. 515–541, 1917.

[2] Gibson, Geol. Surv. of Ala., Report on Murphrees Valley, 1893, p. 121.

[3] Mo. Geol. Surv., XI, p. 186, 1896.

G. P. Merrill[1] has also noted its occurrence in small quantities associated with kaolin, in narrow veins in the decomposing gneissic rock near Stone Mountain, Ga.

The following four analyses[2] represent the composition of halloysite from different localities:

ANALYSES OF HALLOYSITE

	I	II	III	IV
Silica (SiO_2)........	39.30	40.70	42.91	42.00
Alumina (Al_2O_3)....	38.52	38.40	38.40	20.12
Lime (CaO)........	0.75	0.60	0.60	2.81
Magnesia (MgO)...	0.83	1.50	1.5	2.01
Ferric oxide (Fe_2O_3).	1.42	....	....	8.53
Manganese.........	0.25			
Water (H_2O).......	19.34	18.00	18.00	24.00
Potash (K_2O)......	....	....	....	0.50
	100.41	99.20	101.41	99.97

I. Elgin, Scotland.
II. Steinbruck, Styria.
III. Detroit Mine, Mono Lake, Calif.
IV. Striegau, Silesia.

It will be noticed that none of these agree very closely with the composition given by Dana except III. If No. IV is halloysite, it evidently has considerable impurities.

The kaolin found near Leaky, Edwards County, Tex.,[3] appears to be of intermediate composition between kaolinite and halloysite, and may be a mixture of the two, although petrographic evidence is lacking.

A most detailed description of halloysite has been given by E. S. Larsen and E. T. Wherry of two samples collected from the upper workings of the fluorite mine at Wagon Wheel Gap, Colo.[4] One has essentially the composition of kaolinite, but is sensibly isotropic with $n = 1.557$. The other, which is white and opaline to dull, with a hardness of 2, and $n = 1.470 \pm \cdot 010$ had the following properties:

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[1] Non-metallic Minerals, p. 225.

[2] I–III, *ibid.*; IV, Zellner, Neues Jahrb. Min., 1835, p. 467.

[3] See description of Texas clays.

[4] Jour. Wash. Acad. Sci., VII, pp. 178, 180, 1917.

Analyses of Halloysite from Wagon Wheel Gap, Colo.

	I	II	III	IV
Al_2O_3	35.75	35.41	35.58	34.66
Fe_2O_3	Tr.	Tr.	Tr.	
CaO	.80	.73	.77	
MgO	Tr.	Tr.	Tr.	
K_2O	Tr.	Tr.	Tr.	
Na_2O	.10	.09	.10	
SiO_2	39.95	40.22	40.09	40.90
H_2O below 100° C.	8.55	8.66	10.73	12.22
H_2O 100°–400° C.	2.15	2.10		
H_2O above 400° C.	12.85	12.91	12.88	12.22
	100.15	100.32	100.15	100.00

I. II. Analyses of halloysite from Colorado. E. T. Wherry, analyst.
III. Average of I and II.
IV. Theoretic composition for $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O \cdot 2Aq$.

The following changes in optical properties were found to accompany the loss of water:

History of mineral	Total H_2O (approximate)	Optical character	n
As first examined two months after collecting.	25	Isotropic.	1.470 ± .010
After standing six months in a loosely stoppered bottle.	20	Isotropic.	1.542 ± .005
Heated for 4 hours to 65° C. This has the composition and index of the "isotropic kaolinite" from the same locality which is evidently only a halloysite low in H_2O.	15	Isotropic.	1.555 ± .003
Ignited powder, after standing 1 month.	0	Partly isotropic, partly birefracting due to strain.	1.541 ± .003
Powder ignited, quickly cooled, and immersed in index medium.	0	In large parts isotropic but some fragments have birefringence of 0.01 with large axial angle.	1.535 ± .005

The loss in water of the Colorado halloysite determined by heating the coarse powder in a covered platinum dish is given below. The time of heating is not stated.

Loss of Water of Colorado Halloysite on Heating

Temperature	Per cent loss	Total
20° C.	Started	
30	6.40	
40	.90	
50	.75	8.60
60	.50	
100	.05	
110	.00	
150	.10	
200	.40	2.10
300	.60	
400	1.00	
Ignition	12.90	12.90
		23.60

Some of the material kept in a bottle three months, near H_2SO_4, lost 5 per cent.

The authors note that the chemical analyses combined with the optical examination indicate that the material called halloysite is the amorphous mineral corresponding to crystalline kaolinite, holding through capillarity or adsorption more or less excess water.

This same view is expressed by Cayeux.[1]

Mellor[2] on the other hand seems to consider halloysite and kaolinite as two distinct minerals, for he observes that they are readily distinguishable by their heating curves, since halloysite shows no important thermal change at 500° C.

That some caution must be used in identifying clays as halloysite even though they may show the characteristic appearance of that material is indicated by the following three analyses of so-called halloysites from southern states, all of which were dense white, with a conchoidal fracture, and waxy luster.

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[1] Études Pétrographique des Roches Sédimentaires. Text., pp. 229–233.

[2] Trans. Ceram. Soc. (Eng.), XVI, p. 73–84, 1917.

ANALYSES OF SO-CALLED HALLOYSITES

	I	II	III
SiO_2	35.82	43.30	43.18
Al_2O_3	44.38	39.94	39.21
Fe_2O_3	Tr.	Tr.	.15
CaO	0	0	0
MgO	Tr.	.21	Tr.
Na_2O	1.18	.25	.08
K_2O	0	0	0
H_2O below 108° C.	1.61	1.28	3.39
H_2O above 108° C.	16.63	15.04	14.23
	99.62	100.02	100.24
Sp. gr.	2.497	2.441	2.46

I. Sedimentary deposit, Chattooga County, Ga.
II. Sedimentary deposit, Fort Payne Chert, Alabama.
III. Residual deposit, Grubb mines, near Roanoke, Va.

Number 1 contained very small but identifiable crystals of gibbsite in cracks and on the surface.

P. A. van der Meulen, who described them,[1] points out that all three run too high in alumina for halloysite and suggests that they represent mixtures of kaolinite and gibbsite.

Dehydration determinations were made on I and II at 50° C. intervals and it was found that I lost about 6 per cent of water at 300° C., while II lost only 2 per cent. In both most of the remaining water was lost at 500° C., although the last trace was not removed until about 900° C.

The proportions of the two minerals were calculated as follows:

	I	II
Kaolinite	77.03	93.12
Gibbsite	21.32	4.83
Excess water	....	1.63
	99.35	99.58

Clayite.—This name was suggested by J. W. Mellor in 1908 [2] to apply to what he regarded as an amorphous variety of kaolinite, whose identity may seem by some to be established on rather uncertain evidence, viz., the heating curve of the clay.

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[1] Amer. Jour. Sci., Ser. IV, XLIII, pp. 140–144, 1917.

[2] Trans. Ceram. Soc. (Eng.), VIII, p. 23, 1908.

As pointed out by Mellor this curve in the case of clayite shows an endothermal critical point or terrace at 150° C., and a second one at 500–600° C., while there is an exothermal critical point or hump in the curve at 900° C.

It agrees with the heating curve of kaolinite, except for the terrace at 150° C. It differs from halloysite, according to Mellor, in that this mineral shows no terrace between 500–600° C.

Mellor says[1] that the critical point at 150° C. indicates that these clays contain a colloidal substance which loses its water at this temperature. "This substance might be halloysite, colloidal silicic acid or colloidal clayite." In the first two cases the curve of clayite can be regarded as having been developed by the superposition of the curve of kaolinite with that of halloysite or silicic acid, but he thinks it doubtful if either supposition is correct.

J. A. Howe[2] considers that the term clayite is not very satisfactory as much of Mellor's clayite is in fact crystalline as can be easily seen when it is examined under suitable conditions.[3]

Montmorillonite.—A name given by Salvetat[4] to a rose red, clay-like mineral forming nests in a brown clay at Montmorillon, France. Salvetat's analysis is: SiO_2, 49.4; Al_2O_3, 19.7; Fe_2O_3, .8; MgO, .27; CaO, 1.5; Alkalies, 1.5; H_2O, 25.67 = 98.84.

H. Leitmeier[5] described a yellow clayey mineral from Bulgaria under this name, and stated that the microscopic examination showed it to be a gel and completely isotropic, as well as being difficultly soluble even in hot HCl. Part of it was pisolitic. After three years' standing in the laboratory it was found that the greater part of the material was crystalline, with low double refraction and N_m = about 1.51. It was slightly soluble in HCl but completely so in H_2SO_4 after long heating. The analysis of the crystalline material is: SiO_2, 50.14; Al_2O_3, 19.74; Fe_2O_3, 4.14; CaO, 1.26; MgO, 2.28; H_2O, 22.61 = 100.17.

Leitmeier considers part of the Fe_2O_3 as replacing Al_2O_3, leaving the balance as well as MgO and CaO, as impurities. He then figures the formula as $Al_2O_3 \cdot 4SiO_2 \cdot 6H_2O$.

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[1] Trans. Ceram. Soc. (Eng.), XVI, p. 77, 1916–17.

[2] A Handbook to the Collection of Kaolin, China Clay and China Stone in the Museum of Practical Geology, London, 1914.

[3] Even though the mineral described by Mellor as clayite proved to be a valid species, the name could not be retained as it was applied years ago to a variety of Tetrahedrite. See Dana, System Mineralogy, p. 141, 6th ed., and Taylor, W. J., Proc. Acad., Phila., p. 306, 1859; Binns, Trans. Amer. Ceram. Soc., V, p. 14, 1912.

[4] Ann. Chem. Phys., XXI, p. 376, 1847.

[5] Zeitschr. f. Kryst, LV, p. 353–371, 1916.

He quotes four other analyses of so-called montmorillonite in which $SiO_2 : Al_2O_3$ ratio varies from 4.07–4.20, but they all contain notable amounts of impurities, and the water varies from 10.28 to 26.00 per cent.[1]

Dana quoting LeChatelier gives its composition as $H_2Al_2Si_4O_{12} + nH_2O$. He remarks that its properties are not definitely worked out, and published analyses show considerable variation. Stolpenite and Steargillite are given as varieties by Dana.[2]

Ross and Shannon [3] give the formula of montmorillonite as $(MgCa)O \cdot Al_2O_3 \cdot 5SiO_2 \cdot nH_2O$; its physical form as micaceous, and its crystal form as orthorhombic. Their analyses which were made on material obtained by washing the impurities out of bentonite, indicate that its composition agrees closely with material from Montmorillon, France. The MgO content, however, is notably higher than that in Salvetat's analysis given on p. 71.

Montmorillonite has also been described by Brush and Dana [4] as an alteration product of spodumene in pegmatite from Branchville, Conn.

Several of the analyses quoted by Ross and Shannon are given below:

ANALYSES OF MONTMORILLONITE

	I	II	III	IV	V	VI
SiO_2	48.80	49.20	48.60	51.20	48.24	50.60
Al_2O_3	21.08	17.60	20.03	22.14	22.32	17.23
Fe_2O_3	.92	1.60	1.25	. . . .	.36	
MnO	. . . .	. . . .	.16	.18		
CaO	1.36	1.52	1.72	3.72	2.04	3.21
MgO	4.84	5.08	5.24	3.53	6.64	4.56
K_2O . . . . Na_2O	. . . .	. . . .	. . . .	.56		
H_2O	20.92	25.52	21.52	17.08	20.84	24.32
P_2O_5	. . . .	. . . .	. . . .	1.42		

I. Bentonite, Ardmore, S. Dak. Fine portion. Purified by Ross. Shannon, analyst.
II. Bentonite (montmorillonite), Fort Steele, Wyo. Purified by Ross. Shannon, analyst.
III. Montmorillonite, Montmorillon, France. Shannon, analyst.
IV. Montmorillonite from pegmatite, Branchville, Conn. H. L. Wells, analyst.
V. Montmorillonite from pegmatite, Embudo, N. Mex. Shannon, analyst.
VI. Montmorillonite. Theoretical composition to satisfy formula $(MgCa)O \cdot Al_2O_3 \cdot 5SiO_2 \cdot 8H_2O$, with MgO : CaO present in the ratio of 2 to 1.

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[1] See also: D. Lovisato, Atti. Accad. Lincei., XXII, II, p. 670–5; L. Azema, Bull. Soc. franc. min., XXXVI, p. 111–113.

[2] See Dana, Syst. Min., p. 690; Larsen, U. S. Geol. Surv., Bull. 769, p. 113, 1921.

[3] Jour. Amer. Ceram. Soc., IX, p. 77, 1926; see further under Bentonite.

[4] Amer. Jour. Sci., XX, p. 283, 1880.

The proportions of bivalent bases, silica, and trivalent bases, alumina plus ferric iron, is quite constant, the water showing the greatest variability, and some question has been raised as to the manner in which it is held.

The authors state that a large part of the water is driven off at a temperature of 120° C., and much is lost at room temperatures in a desiccator over sulphuric acid and calcium chloride. Indeed samples having lost 12 per cent of moisture at 120° C., regain it in a few hours if exposed to the air of a room.

The following experiments are interesting:

Loss of Water by Montmorillonite Clays

	I	II
100° C.	11.88	14.28
140°	2.00	1.48
450°	2.64	2.44
Red heat	5.00	4.76
	21.52	22.96

I. Montmorillonite, France, per cent.
II. Otaylite, California, per cent.

The clays which had been heated to a constant weight at 140° C. were allowed to stand overnight, and regained 13.88 and 11.56 per cent respectively.

The loss of this water appears to have no effect on the optical properties.

The mean values for the refractive indices are given as, $\alpha = 1.493$, β and $\gamma = 1.516$.

Beidellite.[1]—This is named from the locality of the first occurrence described in detail, Beidell, Colo. It was not separated originally from leverrierite, and was termed clay gouge in one publication.[2]

The formula is given as $Al_2O_3 \cdot 3SiO_2 \cdot xH_2O$, with Al replaced by Fe, and often containing minor amounts of other oxides presumably replacing H_2O. Theory for $x = 4$, a frequent value: SiO_2 51.0 per cent; Al_2O_3 28.7 per cent; H_2O 20.3 per cent = 100.00. It is known only in plates, with indistinct crystal boundaries, often only of microscopic size, and is probably orthorhombic. The luster is vitreous to

[1] Larsen, E. S., and Wherry, E. T., Jour. Wash. Acad. Sci., VII, p. 208, 1917.

[2] Amer. Min., X, p. 141, 1925.

waxy, with color white, reddish or brownish gray. The hardness is less than 2. On wetting, it may become plastic, owing to the entrance of water in innumerable thin films between the plates. The refractive indices of the original beidellite are variable with conditions and methods of measurement, and increase on standing in the immersion liquids to $\alpha = 1.494$, β and $\gamma = 1.536$, which may be taken as standard, but specimens usually rich in iron oxide give higher indices. Beidellite is biaxial, with a small axial angle, $2E$ usually $= 16°$ to $24°$, $2V = 9°$ to $16°$, though approximately uniaxial in some specimens. The alumina-silica ratio is 1 : 3 with about 4 molecules of water, and it is said to belong in a mineral group lying with respect to the alumina-silica ratio, between the kaolinite and the pyrophyllite groups. The colloidal member of the group is apparently steargillite (grouped by Dana under Montmorillonite), and the crystallized member anauxite, although both of these are said to need further study.

The optical properties of beidellite from several localities are given below:[1]

Locality	α	β, γ	$\alpha - \gamma$	$2V$	$2E$	Optical character	Extinction.	Color
Beidell, Colo.	1.494	1.536	0.042	9°–16°	16°–24°	....	....	Gray buff
Owhyee Co., Idaho	1.448	1.527	0.039	Small biax.	....	....	....	White
Nashville, Ark.	1.517	1.549	0.032	"	....	....	....	Gray to light gray
Spokane, Wash.	1.523	1.572	0.051	"	....	....	....	Pistachio green
Wagon Wheel Gap, Colo.	1.495	1.537	0.042	"	....	....	....	Gray

Beidellite has been described from Beidell, Colo.;[2] Black Jack vein, Carson district, Owyhee County, Idaho;[3] Manhattan, Nev., in volcanic rocks;[4] in tuffs of southwestern Arkansas;[5] and in certain schists of Michigan and Wisconsin.[6]

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[1] Ross, C. S., and Shannon, E. V., Jour. Wash. Acad. Sci., XV, p. 467, 1925.

[2] Larsen, E. S., and Wherry, E. T., Jour. Wash. Acad. Sci., VII, p. 208, 1917.

[3] Shannon, C. V., Proc. U. S. Nat. Mus., LXII, 1923.

[4] Econ. Geol., XVI, p. 1, 1921.

[5] Miser, H. D., and Ross, C. S., Amer. Jour. Sci., IX, p. 119, 1925.

[6] Corbett, C. S., Amer. Jour. Sci., X, p. 247, 1925.

The following analyses of beidellite clays are given by Ross and Shannon.[1]

ANALYSES OF BEIDELLITE CLAYS

	I	II	III	IV
SiO_2	45.52	47.28	45.32	50.85
Al_2O_3	27.52	20.27	27.84	28.81
Fe_2O_3	2.80	8.68	.80	
CaO	.52	2.75	2.76	
MgO	3.00	.70	.16	
K_2O	....	Tr.	.12	
Na_2O	....	.97	.10	
H_2O	19.62	19.72	22.64	20.34
	98.96	100.37	99.64	100.00

I. Nashville, Howard County, Ark. Fine separation product. Shannon, analyst.
II. Beidellite, "leverrierite" gouge clay from Beidell, Saguache Co., Colo.
III. Beidellite, "leverrierite" gouge clay, Black Jack vein, Carson Dist., Owhyee County, Idaho.
IV. Theoretical alumina end member to satisfy $Al_2O_3 \cdot 3SiO_2 \cdot 4H_2O$.

Allophane.—This was originally described by Stromeyer and Hausmann from Grafenthal, near Saalfeld.[2]

It is commonly referred to as a clay mineral, the formula of Dana being $Al_2O_3 \cdot SiO_2 + 5H_2O$, while Larsen gives it as $Al_2O_3 \cdot 2SiO_2 \cdot nH_2O$. The former would correspond to: SiO_2, 23.8; Al_2O_3, 40.5; H_2O, 35.1.

It has been variously described as hyaline, stalactitic, pulverulent, and waxy, and of different colors.

The gravity is given as 1.85–1.89, $H = 3$, $n = 1.47$–1.49.

It gelatinizes with HCl and is infusible before the blowpipe.

There is some difference of opinion however as to the true nature of the material called allophane.

Stremme[3] believes that the physical and chemical properties of allophane, including halloysite and montmorillonite are closely allied to artificial mixtures of colloidal Al_2O_3 and SiO_2 obtained by the simultaneous precipitation from aqueous solutions of the salts of SiO_2 and Al_2O_3, and hence cannot be regarded as true silicates. Mellor[4] appears to agree with this view.

These views were disputed by S. J. Thugutt,[5] mainly on the ground that the weak blue coloration which these substances give with cobalt nitrate shows the absence of free alumina.

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[1] Jour. Amer. Ceram. Soc., IX, p. 94, 1926.

[2] Howe, J. A., l.c., p. 162.

[3] Centralb. f. Min., 1908, pp. 622–632 and 661–669.

[4] Trans. Ceram. Soc. (Eng.), XVI, p. 79, 1916–17.

[5] Centralb. f. Min., 1911, p. 97–103, and 1912, p. 35.

To this Stremme [1] makes the rejoinder that the cobalt nitrate test for alumina can be depended on only when the alumina compound is fairly free from iron oxide.

Wherry has suggested that colloidal hydrous-aluminum silicates, with a ratio $Al_2O_3 : SiO_2$ from 1 : 1.5 to 1 : 0.25 be called allophanite.[2]

There is always some doubt as to whether these amorphous clay minerals are definite species or simply adsorption compounds of colloidal silica and alumina with variable amounts of water.[3]

Newtonite.—This mineral, also first described by Brackett and Williams,[4] was found as scattered lumps in a dark gray clay from Newton County, Ark. It was described as a soft white compact homogeneous substance, made up of minute microscopic crystals, of approximately rhombohedral shape.

Its composition is given as $Al_2O_3 \cdot 2SiO_2 \cdot 5H_2O$ = SiO_2, 38.5; Al_2O_3, 32.7; H_2O, 28.8. Sp. gr., 2.37.

Larsen [5] describes it as made up of " very minute square pyramids which have a nearly square outline when lying on the pyramid face. Fragments on a pyramid face show Z' bisecting the acute angle of the rhombic outline, perceptibly uniaxial, optically +. Probably tetragonal. $\omega = 1.560$, $\epsilon = 1.58$. Sp. gr., 2.37.

More recently W. F. Foshag [6] has obtained some samples of this material from the original locality, and finds that on analysis it gives: SO_3, 34.92; SiO_2, .96; Al_2O_3, 38.56; CaO, .78; MgO, .39; K_2O, 8.23; Na_2O, .80; H_2O, 15.15. The mean index is 1.58. He concludes that the chemical composition, physical and optical properties indicate that the " newtonite " is not a species, but is identical with alunite. The analysis given by Brackett and Williams he points out is similar in all respects to that of halloysite, so must have been founded on error in connection with the material analyzed.

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[1] Centralb. f. Min., 1911, p. 205–211.

[2] Proc. U. S. Nat. Mus., XLIX, p. 463–7, 1915.

[3] See also: Rieke, R., Sprechsaal, XLIV, p. 637, 653, 1911; Keppeler, G., *ibid.* XLVI, p. 445, 1913; Wohlin, R., *ibid.*, XLVI, p. 719, 733, 749, 767, 781, 1913; Sokoloff, A. M., Tonind. Zeit., XXXVI, p. 1107, 1912; Arnio, B., Centralb. Min., 1914, p. 69–75; Samoilov, V. and Chervyakov, I. I., Bull. Acad. Sci., Petrograd, 1915, p. 197–204; Mikolaievskii, F. A., Bull. Acad. Sci., St. Petersburg, 1914, p. 147–50.

[4] Amer. Jour. Sci. (3), XLII, pp. 11–21, 1891.

[5] U. S. Geol. Surv., Bull. 679, pp. 115 and 187, 1921.

[6] Amer. Mineral, XI, pp. 33–5, 1926.

Rectorite.[1]—This was described by R. N. Brackett and J. F. Williams, as a new hydrous-silicate of alumina. When pure it was " a soft, white mineral occurring in leaves or plates and resembling very closely in form that variety of asbestos known as mountain leather, and at the same time having somewhat the soapy appearance of steatite."

The authors after throwing out 4.3 per cent of MgO, CaO, Fe_2O_3 and alkalies, recalculate the analysis and give the formula as:

$$Al_2O_3 \cdot 2SiO_2 \cdot H_2O = SiO_2,\ 50.0;\ Al_2O_3,\ 42.5;\ H_2O,\ 7.5.$$

Leverrierite.—Dana gives this as a variety of kaolinite, after Termier,[2] with a formula $2Al_2O_3 \cdot 5SiO_2 \cdot 5H_2O$. Its other properties are: $H = 1.5$; Sp. gr., 2.3–2.4; Optically $-$, Ax. pl. $\parallel$ b (010); Bx. $\perp$ c; Ax. angle 45°–52°; $\beta = 1.6$; $\gamma - \alpha = .0075–.0082$.

Termier[3] in describing a specimen from France notes its occurrence as prismatic crystals, often bent and vermiform, with perfect cleavage perpendicular to the long dimension of the prisms.

The analysis given by him is: SiO_2, 46.79; Al_2O_3, 34.47; CaO, 4.53; Ignition loss, 13.21. It is not known that the material was perfectly pure.

Larsen and Wherry [4] described under leverrierite an aluminum silicate mineral occurring as gouge clay adjoining metalliferous veins, but now consider that it should be called beidellite. They state [5] that in their belief it is better to restrict the name leverrierite to vermicular material, with the alumina-silica ratio near 1 : 2.

Cayeux [6] considers leverrierite so nearly like kaolinite as to class it as a variety rather than a distinct mineral species. He refers to its frequent occurrence in the Cretaceous rocks of France, and thinks that it has been formed in place and is not a detrital mineral.

Pyrophyllite.—$Al_2O_3 \cdot 4SiO_2$. H_2O, or SiO_2, 66.7; Al_2O_3, 28.3; H_2O,5; although a hydrous aluminum silicate appears to have been rarely identified in clay.

The properties are given by Larsen as: α, 1.552; γ, 1.6; β, 1.588; $2V$ dispersion, 57°; $\rho > v$ weak; $X = c$; $Z \parallel$ length; orthorhombic, H, 1–2. Sp. gr., 2.8–2.9. Dehydration tests are given on p. 89.

Schröetterite.—An uncertain clay mineral of amorphous character, and said by Dana to resemble allophane in appearance. Its $H \cdot$ is 3–3.5

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[1] Amer. Jour. Sci. (3), XLII, pp. 11–21, 1891.

[2] Compt. rend., CVIII, p. 1071, 1889.

[3] Ann. d. Mines, XVII, p. 372, 1890.

[4] Jour. Wash. Acad. Sci., VII, pp. 208–217, 1917.

[5] Jour. Wash. Acad. Sci., XV, p. 465, 1925.

[6] Étude Pétrographique des Roches Sédimentaires, Text., pp. 229–233.

Sp. gr., 1.95–2.05, and $n = 1.584$ (Larsen). Composition $8Al_2O_3 \cdot 3SiO_2 \cdot 30\,H_2O$, or SiO_2, 11.7; Al_2O_3, 53.1; H_2O, 35.2. It appears to be present in the indianaite deposits of Lawrence County, Ind. (See under Indiana.)

Indianaite.—This material though listed by Dana and others as a mineral, has no right to be classed as such, for reasons given below:

It represents a peculiar type of clay found along the contact of the Pottsville sandstone and the underlying Chester shale, the type occurrence being near Huron, Lawrence County, Ind., but it has been found as far north as Owens County (see Indiana) and occurs to the southward in Kentucky (see Kentucky). The material is very fine grained, waxy or earthy in lustre, the former being sometimes blue but fading out on exposure to the air. Occasionally there are present botryoidal or granular masses of hyaline material. The indianaite is placed under halloysite by Dana,[1] and called allophane in the Indiana[2] Survey report.

Of the following analyses, No. I is given by Dana, and No. II by the Indiana Survey, Nos. III (halloysite) and IV (kaolinite) are for comparison.

ANALYSES OF INDIANAITE, HALLOYSITE, AND KAOLINITE

	I *	II	III	IV
Silica (SiO_2)	43.25	44.75	43.5	46.3
Alumina (Al_2O_3)	39.92	38.69	36.9	39.8
Ferric oxide (Fe_2O_3)	....	.95		
Lime (CaO)	.69	.37		
Magnesia (MgO)		.30		
Potash (K_2O)	.59	.12		
Soda (Na_2O)		.23		
Water (H_2O)	15.52	15.17	19.6	13.9

* The moisture has been left out, and the analysis recalculated to 100 per cent.

While the percentage of combined water in these analyses is higher than in kaolinite, and the silica lower, still they approach no more closely to those given for halloysite than they differ from similar constituents of kaolinite. However, in view of the composite character of the material, these analyses have little significance.

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[1] System of Mineralogy, 688, 1892.

[2] Ind. Geol. Surv., 29th Ann. Rept.

That Indianaite is not a single mineral is shown by a petrographic examination, made by R. E. Somers.[1]

The massive waxy material contains a number of large flakes which are nearly or quite isotropic, except for minute inclusions. There are also numerous spherulite like grains showing the interference colors of kaolinite.

The earthy variety exhibits numerous radiating bunches and even spherulites of a hydromica, possibly sericite. Kaolinite is also abundant.

Some of the hyaline material was isotropic with an index of 1.50–1.53, and gelatinized with hydrochloric acid, a property said to be common to both allophane and schroetterite.

The following analyses are not without interest:

Analyses of Indianaite and Associated Minerals

	I	II	III	IV	V
SiO_2......	43.47	10.70	23.80	11.70	43.5
Al_2O_3.....	38.03	54.53	40.50	53.10	36.9
H_2O+100° C....	14.73	29.48	35.70	35.20	19.6
Fe_2O_3.....	.25	.37			
FeO......					
H_2O−100° C....	3.82	5.26			

I. Waxy clay, Gardner Mine, G. Steiger, analyst.
II. Hyaline material, Gardner Mine, G. Steiger, analyst.
III. Allophane, Dana, Syst. Min., 6th ed., p. 693, 1912.
IV. Schroetterite, ibid., p. 694.
V. Halloysite, ibid., p. 688.

A comparison of the above analyses shows that the hyaline material resembles schroetterite, but the waxy clay agrees more closely with halloysite than allophane. It is not pure halloysite, since the microscopic examination shows that the material contains some kaolinite and hydrous mica.

A similar type of clay apparently allied to indianaite has been described by J. H. Gardner from the Mississippian near Brownsville, Edmonson County, Ky.[2] There, underlying the Conglomerate sandstone is a white waxy clay with conchoidal fracture and said to resemble indianaite. It grades down into a hard brown layer thought to be bauxite (Fig. 34) with admixed wavellite.

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[1] U. S. Geol. Surv., Bull. 708, p. 156, 1921.

[2] Ky. Geol. Surv., Bull. 6, p. 50, 1905.

The following analyses, which are taken from Gardner, have been recalculated to 100 per cent after subtracting an appreciable percentage of moisture given under each:

ANALYSIS OF CLAYS FROM EDMONSON CO., KY.

	I	II	III
Silica (SiO_2)	44.69	45.35	22.81
Alumina (Al_2O_3)	38.17	37.64	46.15
Ferric oxide (Fe_2O_3)	.47	.68	1.41
Lime (CaO)	.40	.36	.41
Magnesia (MgC)	.55	.56	.45
Potash (K_2O)	.09	.24	.35
Soda (Na_2O)	.08	.09	
Phosphoric acid (P_2O_5)	.21	.23	4.27
Titanic acid (TiO_2)	Tr.	Tr.	Tr.
Sulphur trioxide (SO_3)	Tr.	Tr.	.30
Ignition	15.30	14.80	23.82
Total	99.96	99.95	99.97

I. White clay.
II. Waxy clay.
III. Bauxite-Wavellite mixture.

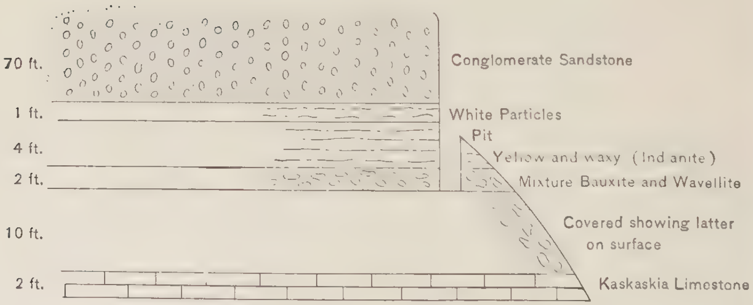

FIG. 34.—Section in Mississippian near Brownsville, Ky., showing occurrence of indianaite and bauxite. (After Gardner, Ky. Geol. Surv., Bull. 6, 1905.)

Pholerite.—This term was first applied by Guillemin in 1825[1] to a pure white pearly substance, occurring in the form of small hexagonal scales, soft and friable to the touch, adherent to the tongue, and giving a plastic mass with water. Similar occurrences were noted later by J. L. Smith[1] in 1859, by A. Knop,[2] and by L. L. Konnick.[3]

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[1] Ann. des Mines, XI, p. 489.

The composition of pholerite is: Silica (SiO_2) 39.3, alumina (Al_2O_3) 45, water (H_2O) 15.7, which corresponds to a chemical formula of $2Al_2O_3 \cdot 3SiO_2 \cdot 4H_2O$.

Dana[4] classes this under kaolinite, but, in view of the fact that the pholerite has been found in crystalline form, this hardly seems reasonable.

So far as the author knows little crystallized pholerite has been described from the United States, but Wheeler has pointed to its probable presence in some of the Missouri flint-clays,[5] in which the silica-alumina ratio ranged from 0.94 to 1.15. Now, since this ratio in kaolinite is 1.16 and in pholerite 0.81, it seems quite probable that in some at least of the Missouri clays there is a mixture of kaolinite and pholerite present.

Cook, in his report on the New Jersey clays,[6] gives 32 analyses in which the combined silica has been separated from the sand, and of these 21 seem to indicate the presence of some pholerite, their silica-alumina ratio ranging from 0.94 to 1.15.

If this explanation is correct, then pholerite is no doubt present in many other fire-clays, and perhaps even some kaolins. The writer has questioned whether the presence of bauxite with the kaolinite might not give a mixture with a high alumina percentage similar to that shown by pholerite.

A. Ledoux[7] has described a pholerite from Quenast, and states that it is triclinic, with low index of refraction and birefringence. He further states that it is almost identical in its optical properties with nacrite and while differing in crystallization from kaolinite, is like it in composition. This latter statement may be open to dispute.

Collyrite.—The name was given by Karsten[8] to a white clay-like material, found in sandstone near Weissenfels, Saxony. It had a greasy feel, and shiny lustre. It is also said to have been found in the chalk near Brighton, England, as well as in the Pyrenees and Hungary. The formula is given by Dana as $2Al_2O_3 \cdot SiO_2 \cdot 9H_2O$.

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[1] Amer. Jour. Sci., ii, XI, p. 58.

[2] Neues Jahrb. Min., 1859; also Johnson and Blake, Amer. Jour. Sci., XLIII, p. 361, 1867.

[3] Zeitschr. f. Kryst. u. Min., II, p. 661

[4] Syst. Min., 1893, p. 685.

[5] Mo. Geol. Surv., XI, p. 50, 1897.

[6] N. J. Geol. Surv., 1878.

[7] Bull. Soc. Belge geol., XXVII, p. 96–8, 1913, and Neues Jahrb. Min. Geol., 1915, I, Ref. 183.

[8] Tab., XXX, p. 73, 1800.

Nontronite.—$H_4Fe_2Si_2O_9$, the ferric equivalent of kaolinite,[1] described by Weinschenk, may occur in clays, but is rarely referred to or identified. It is less stable than kaolinite, being easily decomposed, either by acid or alkaline solutions, yielding limonite as a final product of aqueous action.

Nacrite.—This name was given by A. Brogniart to a micaceous mineral which Haug had previously likened to lepidolite.[2] Later A. Breithaupt [3] used the term for what appeared to be an earthy talc occurring as snowwhite or yellowish-white plates, collected in fanshaped or reniform masses, and having a pearly lustre. He stated that its composition was close to kaolinite. An analysis of material from the ore veins at Freiberg, Saxony,[4] gave: SiO_2, 47.93; Al_2O_3, 37.70; H_2O, 14.06.

Both Dana [5] and Doelter [6] give nacrite as a synonym of kaolinite, while Johnson and Blake [7] state that it is identical with pholerite. On the other hand, J. W. Mellor,[8] quoting from A. B. Dick, states that it is negative, but that otherwise its properties and composition are the same as kaolinite from Anglesea.

Classification of clay minerals.—In looking through the literature one cannot fail to notice the large number of hydrous aluminum silicates which have been described, separate species having sometimes been based on a chemical analysis of a limited amount of material, and there being furthermore no definite knowledge that the substance was pure. A petrographic examination made prior to the chemical analysis, would be of great assistance.

J. A. Howe, in his Handbook on Kaolin, gives the names of sixty-one hydrous aluminum silicates, which had been added to the literature up to 1914, and E. T. Wherry [9] has added to the list. The validity of many of these species may be questioned.

Several attempts have been made to classify the hydrous aluminum silicates, and several of these are given below, although none of them can be regarded as satisfactory.

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[1] Zeitschr. Kryst. u. Min., XXVIII, p. 150, 1897.

[2] Min., I, p. 505, 1807.

[3] Char., 94, p. 318, 1832, and J. W. Mellor, Trans. Ceram. Soc. (Eng.) XVI, p. 74, 1916–17.

[4] Doelter, C., Mineral Chem., II, p, 125, 1917, and quoted from Müller, R., and Breithaupt, A., Berg. u. hütt. Zeit., XXIV, p. 336, 1866.

[5] Sys. Min., p. 685.

[6] l. c.

[7] l. c.

[8] Trans. Ceram. Soc. (Eng.), XVI, p. 74, 1916–17.

[9] Proc. U. S. Nat. Mus., XLIX, p. 463.

Le Chatelier's Classifications.[1]—H. Le Chatelier [2] in studying the action of heat on certain clays, emphasized the fact that in spite of the common occurrence and industrial importance of the hydrated aluminum silicates little is known as regards their chemical constitution. They generally form mixtures so complex that analysis alone furnishes no precise data as to their nature, and he suggests that by studying the temperature of dehydration of these bodies, it may be possible to identify a small number of chemical species, and to distinguish the presence of each of them in different mixtures. Le Chatelier states that if a small quantity of clay is rapidly heated there occurs at the moment of dehydration a retardation in the rise of temperature, and this point may be utilized for establishing a distinction between the various hydrated aluminum silicates.

As a result of his experiments he recognized the following groups:

1. Halloysite ($2SiO_2 \cdot Al_2O_3 \cdot 2H_2O + Aq$). Shows a retardation in the rate of rise of the temperature between 150° and 200° C., a second one at 700° C., followed by a sudden acceleration at 1000° C.
2. Allophane ($SiO_2 \cdot Al_2O_3 + Aq$). Retardation between 150° and 220° C., and acceleration at 1000° C.
3. Kaolin ($2SiO_2 \cdot Al_2O_3 \cdot 2H_2O$). Shows retardation towards 770° C., and a slight acceleration towards 1000° C.
4. Pyrophyllite ($4SiO_2 \cdot Al_2O_3, \cdot H_2O$). The first distinct retardation occurs at 700° C., and a second, but less-evident one, at 850° C.
5. Montmorillonite ($4SiO_2,Al_2O_3,H_2O + Aq$). First retardation at about 200° C., a second at 770° C., and a third less-marked one at 950° C.

At a later date Le Chatelier altered his classification and made the following three groups: [3] 1. Allophane group; 2. Kaolinite group, including: (*a*) kaolin formed from igneous rocks; (*b*) clay, both capable of forming plastic paste with water, and (*c*) halloysite, nonplastic; 3. Pyrophyllite group, including montmorillonite.

H. Stremme [4] suggested that clay minerals be classified according to: (1) solubility in HCl, or (2) solubility in H_2SO_2. He stated that they are crystalline to crypto-crystalline, amorphous, colloidal or plastic.

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[1] Reference may also be made to work of J. W. Mellor (Trans. Ceram. Soc. (Eng.), XVI, p. 78, 1917) who proposes to differentiate a series of hydrous aluminum silicates on the basis of their heating curves.

[2] Compt. rend., CIV, p. 1443, 1887; also Ding. polyt. Jour., CCLXV, p. 94, 1887.

[3] La Silice et les Silicates, Paris, 1914.

[4] Zeit. f. prak. Geol., XVI, p. 124, 1908.

In 1916, L. Cayeux[1] divided the clay minerals as follows:

1. Crystalline clay minerals: Kaolinite, halloysite, and montmorillonite.

2. Amorphous clay minerals: Allophane, collyrite.

E. T. Wherry[2] made a still different grouping, as below:

1. Cimolite group. Mostly soft earthy clays with alumina: silica ratio of 1 : 7.5 to 1 : 2.5. Included in this is montmorillonite.

2. Halloysite group. Mostly soft, earthy clays with alumina : silica ratio of 1 : 2.5 to 1 : 1.5. Included in this are allophane, some kaolinite and pholerite.

3. Allophanite group. Harder, more vitreous, with alumina : silica ratio of 1 : 1.5 to 1 : 0.25. Included are collyrite and schrötterite.

More recently Wherry[3] has proposed a grouping of aluminum silicates, based on their $Al_2O_3 : SiO_2$ ratio, and under each of these ratios, makes a further subdivision of colloids, metacolloids and crystals.

The following extracts from his table may serve as examples:

Colloids	$SiO_2 : Al_2O_3$	Metacolloids	Crystals
Collyrite	1 : 3	Mullite	Mullite (cryst'd)
Allophane	1 : 2	Fibrolite	Sillimanite
Halloysite	1 : 1	Newtonite Nacrite Cryptotilite	Kaolinite
Cimolite	2 : 1	Agalmatolite	Pyrophyllite

This classification is doubtful of universal acceptance: Montmorillonite, for instance, is rejected by Wherry, because the recent studies by Ross and Shannon " have shown that it contains a relatively large and definite amount of essential magnesia."

Aluminum Hydrates

The occurrence of aluminum hydrates in clay is always a possibility, and as pointed out by the writer elsewhere,[4] it is not improbable that some high-alumina clays might be mixtures of kaolinite (or some allied mineral) and some aluminum hydrate, but unless the latter can be definitely identified, such deductions rest on a rather insecure foundation.

M. G. Edwards[5] sought to show from the recalculation of a number of selected analyses, that they might be regarded as mixtures of kaolinite and some aluminum hydrate but his conclusions were not backed up by any petrographic evidence.

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[1] Étude Pétrographique des Roches Sédimentaires, p. 229, 1916.

[2] Proc. U. S. Nat. Mus., XLIX, p. 463, 1915.

[3] Amer. Min., X, p. 140, 1925.

[4] Econ. Geol., IX, p. 402, 1914.

[5] Econ. Geol., IX, p. 112, 1914.

Some high-alumina clays may show the distinctly pisolitic structure[1] characteristic of bauxite, although petrographic examination may show little evidence of either gibbsite or diaspore, but in a few cases these have been definitely identified.

Gibbsite.—This may be abundant in some high-alumina flint-clays and has been definitely identified by Galpin as occurring in the pisolitic flint clays of the Olive Hill district of Kentucky,[2] and by Rogers, from a clay at Morton, Minn.[3]

P. A. van der Meulen[4] has noted it in cracks in a highly-aluminous sedimentary clay from Chatooga County, Ga.

It has also been tentatively identified by G. V. Wilson in the Ayrshire Bauxitic clay of Scotland.[5]

Diaspore.—This mineral has not often been noted in clays, but it is abundant in some flint-clay deposits of central Missouri, in which it may occur as scattered grains, or forming oolites (Fig. 137).[6] It has also been noted as a decomposition product of porphyrite in Japan.[7]

Wherry, who suggests that the material be called *diasporite,* checked its optical properties (biaxial, with indices = 1.70 and 1.75).

R. Wohlin[8] gives the following loss of water on dehydrating diaspore.

LOSS OF WATER BY DIASPORE ON HEATING

Temperature ° C	Per cent H_2O lost	Temperature ° C	Per cent H_2O lost	Temperature ° C	Per cent H_2O lost
150	.02	400	.32	600	14.43
200	.10	450	1.40	650	14.47
250	.10	500	6.62	700	14.52
300	.22	550	12.09	Ignition	14.82
350	.22				

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[1] Shearer, H. K., Ga. Geol. Surv., Bull. 31, 1917.

[2] Trans. Amer. Ceram. Soc., XIV, 301, 1912.

[3] Jour. Geol., XXV, p. 515, 1917.

[4] Amer. Jour. Sci. (4), XLIII, p. 140, 1917.

[5] Memoirs Geol. Surv. Scot., p. 12, 1922.

[6] Wherry, E. T., Amer. Mineralogist, III, p. 154, 1918, and Somers, R. E., U. S. Geol. Surv., Bull. 708, p. 299, 1921; Wysor, D. C., Jour. Amer. Ceram. Soc., VI, p. 501, 1923; Howe and Ferguson, Jour. Amer. Ceram. Soc., VI, p. 496, 1923; Phelps, S. M., ibid., IX, p. 659, 1926.

[7] Jour. Jap. Ceram. Assoc., XXXII, p. 251, 1924.

[8] Sprechsaal, XLVI, p. 767, 1913.

The heating curve shows much greater absorption of heat between 540° and 565° C., and this checks in a general way with the temperature at which the greatest amount of water is lost.[1]

Comparison of aluminum hydrates.—It is of interest in this connection to give the chemical analyses and several physical properties of some diaspore, bauxite and gibbsite clays as determined by R. M. Howe and R. F. Ferguson.[2]

ANALYSES AND PHYSICAL PROPERTIES OF DIASPORE AND GIBBSITE CLAYS

	I	II	III	IV	V	VI	VII
Ignition	28.08	17.90	13.74	13.14	9.88	14.98	14.24
SiO_2	9.70	18.90	13.96	20.50	1.36	17.84	5.34
Al_2O_3	56.31	52.48	67.21	60.89	60.66	61.98	73.70
Fe_2O_3	3.10	4.39	0.75	0.55	23.55	0.47	2.28
TiO_2	2.09	2.68	3.22	3.14	3.85	2.85	3.57
CaO	0.22	3.17	0.22	0.43	0.22	0.22	0.40
MgO	0.52	0.40	0.36	0.31	0.50	0.79	0.16
Alkalies	0.49	0.43	1.16	1.34	0.37	0.38	0.53
Total	100.51	100.35	100.62	100.30	100.39	100.51	100.24
Fusion point cones	41	34	42	40	42	40	42
Shrinkage	8.3	5.5	11.6	5.8	8.4	3.7	10.2
Porosity, cone 3	59.6	47.1	45.4	40.3	53.1	48.0	49.0
Porosity, cone 18	42.9	31.7	38.8	36.7	8.9	31.8	46.3
Burning shrinkage to cone 3	18.0	12.7	8.2	12.2	12.2	16.7	1.3
Burning shrinkage to cone 18	42.6	30.8	29.9	16.3	55.2	38.2	16.3
Source	Ark.	France	Mo.	Mo.	France	France	Mo.

According to R. Wohlin,[3] there are three types of bauxites distinguishable by their heating curves and dehydration temperatures as follows:

1. Dehydration temperature 540° C. (1004° F.), ignition loss 12–14 per cent and with about same composition as diaspore.

2. Dehydration temperature about 310° C. (590° F.), with ignition loss 27–35 per cent. Composition same as gibbsite.

3. Dehydration temperature partly like 1 and partly like 2, ignition loss about 20 per cent. Mixtures of 1 and 2.

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[1] See also Kumazawa, J., Jour. Chem. Ind., Tokyo, XXIII, p. 236, 1920.

[2] Jour. Amer. Ceram. Soc., VI, p. 496, 1923.

[3] Sprechsaal, XLVI, p. 781, 1913; see also Bigot, A., Cer., XXVI, p. 56, 1923; Kurnakov, N. S., and Urazov, G. G., Ann. Inst. Phys.-Chem. Anal. Leningrad, II, p. 296 and 495, 1924.

OTHER MINERALS

Quartz.—This mineral is found in at least small quantities in nearly every clay, whether residual or sedimentary, but the grains are rarely large enough to be seen with the naked eye. They are translucent or transparent, usually of angular form in residual clays and rounded or subangular in sedimentary ones. The quartz grains may be colorless, but are more often colored superficially red or yellow by iron oxide. Nodular masses of amorphous silica, termed chert or flint, are found in some clays. These are not uncommon in many residual clays of the southeastern States, and sometimes appear to have developed in connection with weathering. Quartz pebbles are by no means rare in many sedimentary clays of Mesozoic or Pleistocene age; indeed, most of the sand-grains found in the coarse, gritty surface clays of sedimentary character are quartz. This mineral also forms most of the hard pebbles found in the so-called " feldspar " beds of the Woodbridge district of New Jersey.[1]

Both quartz and flint are highly refractory, being fusible only at cone 35 of the Seger series (see Fusibility), but the presence of other minerals in the clay may exert a fluxing action and cause the quartz to soften at a much lower temperature.

The amount of quartz in clays varies from under 1 per cent in some kaolins or fire-clays to over 50 or 60 per cent in some very sandy brick-clays.

Feldspar.—This mineral is nearly as abundant in some clays as quartz, but, owing to the ease with which it decomposes, the grains are rarely as large.

There are several species of feldspar, which vary somewhat in their chemical composition, and are known by different names, as shown below.

COMPOSITION OF FELDSPARS

Feldspar species	Chemical composition				
	SiO_2	Al_2O_3	K_2O	Na_2O	CaO
Orthoclase	64.70	18.40	16.90		
Albite	68.00	20.00	....	12	12
Oligoclase	62.00	24.00	....	9	5
Labradorite	53.00	30.00	....	4	13
Anorthite	43.00	37.00	....	....	20

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[1] Ries and Kümmel, N. J. Geol. Surv., Fin. Rept., VI, p. 468, 1904.

The fusing-point of feldspar is about cone 9 (see Seger Cones, under Fusibility), but the different species vary somewhat in their melting-points. The feldspar grains may, however, begin to flux with other ingredients of the clay at a much lower temperature. (See under Alkalies.) The feldspars weather rather easily. Plagioclase is usually less resistant than orthoclase, and this in turn apparently less so than microcline.[1]

The addition of feldspar to aluminous fire-clays of high porosity at 900° C. and short porosity range, was found to diminish the shrinkage up to 1000°–1100°C. Increasing the feldspar reduced the porosity at temperatures exceeding 1100°–1200° C.[2]

Wilson states that between feldspar and kaolin there seems to be a eutectic at 2–3 per cent kaolin, and another and much greater one at about 10 per cent kaolin. Near these eutectics the rate of deformation is much faster.[3]

Mica.—This is one of the few minerals in clay that can often be detected with the naked eye, for it occurs commonly in the form of thin, scaly particles whose bright, shining surface renders them very conspicuous, even when small. Very few clays are entirely free from mica, even in their washed condition, for, on account of the light scaly character of the mineral, it floats off with the clay particles. Some clays are highly micaceous, but such are rarely of much commercial value.

There are several species of mica, all of rather complex composition, but all silicates of alumina, with other bases. Two of the commonest species are the white mica or muscovite, $H_3KAl_3(SiO_4)_3$ = (SiO_2 45.2, Al_2O_3 38.5, K_2O 11.8, H_2O 4.5), and the black mica or biotite $(H_1K)_2(Mg,Fe)_2(Al,Fe)_2(SiO_4)_3$. Of these two, the muscovite is the most abundant in clay, because it is not readily attacked by the weathering agents. The biotite, on the other hand, decomposes much more rapidly on account of the iron oxide which it contains. Other species of the mica group are no doubt present in some clays. The effect of mica in burning is mentioned under Alkalies.

Fine-grained muscovite (sericite) has been noted by several writers who have examined clays microscopically,[4] although some, like Bertrand, have asserted that true mica [5] does not frequently occur in clays.

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[1] Clarke, F. W., and Steiger, G., U. S. Geol. Surv., Bull. 167, 1900.

[2] Firth and Turner, Jour. Soc. Glass Technol., IV, p. 397, 1920.

[3] Trans. Amer. Ceram. Soc., XV, p. 217.

[4] Galpin, S. L., Trans. Amer. Ceram. Soc., XIV, p. 301, 1912; Somers, R. E., U. S. Geol. Surv., Bull. 708, p. 292, 1921; Schurecht, H. G., Jour. Amer. Ceram. Soc., V, p. 3, 1912.

[5] Recherches et inventions, IV, p. 825–33 and 841–51, 1923.

It is probable, however, that many of the micaceous minerals found in clay had best be called hydromica.

Stuckey,[1] in making a comparative study of sericite and pyrophyllite, ran a series of dehydration tests on the two minerals, the results of which are given below.

Dehydration Temperatures of Sericite and Pyrophyllite

Temperature	Loss of water in per cent	
	Sericite	Pyrophyllite
500–600° C.	2.2	.98
600–700° C.	1.35	1.84
700–750° C.	.39	1.47
750–800° C.	.40	.75
900° C.	....	.20
	4.34	5.24

From the above figures it will be noted that the pyrophyllite seems to lose its water at a slower rate than the sericite.

Some writers have endeavored to determine the percentage of muscovite in a clay from its chemical analysis, but this is far from safe for the reason that there is no means of knowing what proportion of the potash determined on analysis is present as a constituent of muscovite, of orthoclase, or as an adsorbed compound.

Mica if abundant and in megascopic grains seems to reduce the plasticity of the clay, but if the grains are microscopic their effect in this direction is less noticeable. It may also reduce the fusion. According to Rieke [2] muscovite alone has a fusion point equivalent to Cone 13.

When mixed in a clay muscovite appears to act as a flux at different temperatures, according to the size of the grains. If very finely ground, the mica appears to vitrify the body at as low a temperature as Cone 4,[3] but if the scales are larger they will retain their individuality up to Cone 8, or even 10. The latter is true, for example, of the micaceous clay found in the Miocene formation around Woodstown, N. J., a large amount of which is composed of white mica.[4]

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[1] Jour. Amer. Ceram. Soc., VII, 735, 1924.

[2] Sprechsaal, XL, p. 577, 1908.

[3] Trans. Amer. Ceram. Soc., IV, p. 255.

[4] Ries, N. J. Geol. Surv., Fin. Rept., VI, p. 68, 1904.

It was found that if 60 per cent muscovite is added to Zettlitz kaolin, its fusion point was reduced from Cone 35 to 31.

Lepidolite occurs in some clays, as evidenced by the small amounts of lithia which have been occasionally noted.[1]

Hydromica.—This is a distinctly micaceous mineral whose single and double refraction are higher than those of kaolinite, yet not so high as muscovite. It is therefore assumed that there is an isomorphous gradation between muscovite and kaolinite, which is marked by a gradual loss of potash and addition of water, and therefore in the process of weathering hydromica may represent a transition stage towards kaolinite.[2]

As has been pointed out by Somers it is probable that the hydromicas are much more abundant than is supposed by many and his work indicates the mineral to be exceedingly common in many clays. A large proportion of it does not appear though to reduce the refractoriness to any considerable degree.

Hickling [3] has pointed out that the washed china-clay of Cornwall is made up of 90 per cent kaolinite and mica, but that the relative amounts of the two are difficult to estimate. While he refers to the mica as muscovite he remarks that it may be hydrated, and quotes from the observations of Johnstone [4] who found that muscovite changed to hydromuscovite after immersion in pure water or carbonated water for twelve months.

Hydrous Iron oxides.—Hydrous iron oxide is a common constituent of many clays. Its presence when in a finely divided condition is shown by the yellow or brown color of the material, in which case it may be present as a film on the surface of the grains, or possibly adsorbed by them. At other times it may occur as concretionary masses of varying purity and shape, or as stringers and crusts extending through the clay in different directions. The beds of sandstone found in many sand or gravel deposits associated with some clays, are caused by hydrous-iron oxide cementing the grains together.

The hydrated oxide is usually referred to as limonite (and it is used in that sense in this book), but it might include any one of those hydrous iron oxides usually described in the text-books, viz.: Turgite ($Fe_2O_3 \cdot \frac{1}{2}H_2O$), Goethite and Lepidocrocite ($Fe_2O_3 \cdot H_2O$), Hydrogoethite ($Fe_2O_3 \cdot \frac{4}{3}H_2O$), Limonite ($Fe_2O_3 \cdot \frac{3}{2}H_2O$), Xanthosiderite ($Fe_2O_3 \cdot 2H_2O$), and Limnite ($Fe_2O_3 \cdot 3H_2O$).

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[1] N. W. Lord, Amer. Inst. Min. Eng., Trans., XII, 505.

[2] Somers, R. E., U. S. Geol. Surv., Bull. 708, p. 298, 1921.

[3] Inst. Min. Engrs. (Eng.), Trans., XXXVI, 1908–9.

[4] Jour. Geol. Soc. London, XLV, p. 363, 1889; see also Bayley, Econ. Geol., XV, p. 236, 1920.

Posnjack and Merwin[1] state: "Of these goethite alone has been well defined physically, and chemically. Descriptions of lepidocrocite (rubinglimmer) leave a doubt as to its identity with goethite, although Lacroix[2] makes a definite optical distinction. Hydrogoethite has been supposed to contain more water than goethite but in its optical properties is said to be similar to lepidocrocite. The other names in the list have been given because of certain indefinite physical differences associated with plausible but not well-established chemical formulas."

According to these same authors the only existing hydrate is a ferric oxide monohydrate, $Fe_2O_3 \cdot H_2O$, which occurs in two polymorphic forms, goethite and lepidocrocite, and in an amorphous condition, limonite. The latter name they retain for "material which appears to be essentially isotropic ferric-oxide monohydrate with adsorbed capillary water. However, this substance should not be considered a distinct form of ferric oxide monohydrate as the real nature of such substances is uncertain."

Dehydration curves given by Posnjak and Merwin indicate that in two specimens of turgite, the loss was a gradual one up to a maximum of about 250° C. in one case, and about 350° C. in the other. The other samples which they tested all showed a strong loss between approximately 150–250° C., after which there was very little.

It was further found that the hydrous iron oxides were capable of rehydration. Thus, after dehydrating, the substance was left to come to constancy in the room. It was dehydrated again as before, and it was found that the amount of water taken up in the room, was roughly equal to the amount lost in the first portion of the dehydration curves.

The slow dehydration of the turgite, leads to the opinion that it is essentially different from the other hydrated ferric oxides, and the authors suggest that it probably represents "solid solutions of goethite with hematite together with enclosed and adsorbed water."

The hydrous iron oxides are most abundant as a rule in surface clays, especially those which are of a sandy character or sufficiently porous to admit the oxidizing waters from the surface. They are likewise common in the weathered outcrops of many shales, and in residual clays.

Concretions of hydrous iron oxide can often be removed by hand picking. If left in the clay they cause fused blotches which are unsightly and sometimes even cause splitting of the ware.

Hematite, the oxide of iron, is of a red color and may be found in clays, but it changes readily to limonite on exposure to the air and in the presence of moisture.

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[1] Amer. Jour. Sci. (4), XLVII, p. 311–348, 1919.

[2] Mineralogie de la France, 3, 360.

Magnetite, the magnetic oxide of iron, forms black magnetic grains, and, while not common, is sometimes found when the material is examined microscopically. Like the hematite, it changes to limonite.

Siderite, the carbonate of iron, may occur in clay in the following forms: 1. As concretionary masses known as clay-ironstones, ranging in size from a fraction of an inch to several feet in diameter. They are very abundant in some Carboniferous shales, and are often strung out in lines parallel with the stratification of the clay. If near the surface, the siderite concretions often change to hydrous iron oxide. 2. In the form of crystalline grains, scattered through the clay and rarely visible to the naked eye. 3. As a film coating other minerals in the clay. This mineral will also change to limonite if exposed to the weather.

When iron carbonate is in a finely divided condition and evenly distributed through the clay it may give it a blue or slate-gray color.

Siderite may be present in some surface clays, but it is probably of greatest importance in shales, notably those associated with coal-seams, and may occur in either finely divided (disseminated) or concretionary form. It loses its carbon dioxide about 700° C.

Pyrite[1] (FeS_2 = Fe 46.6 per cent, S 53.4 per cent).—This mineral, which is not uncommon in some clays, can be often seen by the naked eye, and is known to the clay-miners in some districts as *sulphur*. It has a yellow color, metallic luster, and occurs in large lumps, small grains or cubes, or again in flat rosette-like forms. Not infrequently it is formed on or around lumps of lignite, showing quite clearly that the carbonaceous matter has reduced some iron sulphate present to sulphide. It is a familiar object to all clay-miners of the Raritan district of New Jersey, and abundant also in many Carboniferous clays.

When exposed to the weather pyrite alters rather easily, first to the sulphate of iron and then to limonite. Clays containing pyrite are not, as a rule, desired by the clay-worker, and in mining the pyritic material is rejected.

Pyrite may be found in almost any clay or shale, but owing to the ease with which it is converted into limonite its formation or permanence in surface clays is rare.

Calcite ($CaCO_3$ = CaO 56.00 per cent, CO_2 44.00 per cent).—This mineral, when abundant, is found chiefly in clays of recent geological age, but some shales also contain considerable quantities of it. It can be easily detected, for it dissolves rapidly in weak acids, and effervesces violently upon the application of a drop of muriatic acid or even vinegar. It is rarely present in grains large enough to be seen with the naked eye, but has been detected with the microscope.[1] It is also possible that the lime carbonate in clays may be in colloidal form.

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[1] In some clays this may be marcasite, the orthorhombic form of FeS_2.

In some clays calcite, as well as some other minerals, may form concretions. Many of the lacustrine and glacial clays found in Wisconsin and Michigan contain large quantities of lime carbonate, and some of those found in other states are highly calcareous. The flood-plain clays mentioned under Texas often carry a high percentage of carbonate of lime.

Residual clays derived from limestone may contain fragments of the parent rock which has not been completely weathered.

Aragonite.—It is not known how abundant this form of calcium carbonate is in clays. A layer of aragonite crystals has been described in the upper Triassic clays of eastern Corbieres.[2]

Dolomite.—This is only occasionally referred to as a constituent of clay, and is rarely present in large amounts.

A peculiar type of clay has been described by Ries from Texas[3] which was made up almost entirely of rhombs of dolomite, .008 mm. across. The material was loess-like in character, but possessed sufficient plasticity to permit molding.

Gypsum ($CaSO_4 \cdot 2H_2O$ = CaO 32.6 per cent, SO_3 46.5 per cent, H_2O 20.9 per cent).—It is doubtful whether this mineral is widely distributed in clays, but it is true that some deposits contain large quantities of it. It may occur in a finely divided condition, or in the form of crystals, plates, or fibrous masses of selenite.

Many shale formations may contain selenite in the form of concretions, plates, or crystals, and the outcrops are sometimes strewn with them. This is a common occurrence in some of the shales of the western United States and Canada. In the east the Salina shale of New York, the Lulbegrud shale of central Kentucky, and some of the clays of the Atlantic coastal plain also exhibit it.

Gypsum when heated to a temperature of between 250° and 400° F., loses three-quarters of its water of hydration.

Montgomery and Graves,[4] on heating crystalline gypsum, pulverized to pass a 100-mesh sieve, found that it lost no water up to 100° C., but that if held four hours between 105° and 107° it lost 20.7 per cent or all of its water. There was no further loss on raising the temperature. The authors claim there is no such compound as $CaSO_4 \cdot \frac{1}{2}H_2O$.

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[1] Wheeler, Mo. Geol. Surv., XI; Buckley, Wis. Geol. and Nat. Hist. Survey, Bull. VII, Pt. I.

[2] Durand, J., Compt. rend., CLVII, p. 59.

[3] Amer. Jour. Sci., XLIV, p. 316, 1917.

[4] Trans. Amer. Ceram. Soc., XVIII, p. 214–222, 1916.

The SO_3, in gypsum-clay mixtures, according to Kramm,[1] is driven off gradually at temperatures up to cone 1. Beyond this point evolution of the gas is rapid. All the SO_3 may be driven off at about 1100° C.

This dissociation temperature of $CaSO_4$ can, it is claimed, be lowered by SiO_2 and Fe_2O_3, to 1000° C. and 1100° C. respectively.[2]

Rutile.—This appears to be a wide-spread mineral in clays, but never occurs in large amounts or in large grains. It usually is observed in the form of microscopic grains or needles, which according to Somers [3] range from about .001–.010 mm. diameter, with the length five or six times the width. They have also been noted by other writers.[4]

Somers states that the rutile grains appear to be unaffected even after the clay has been fired to a temperature of 1300° C.

It is possible that some of the titanium in clay may be due to some other titanium-bearing mineral such as ilmenite, leucoxene or titanite, but they have been rarely recorded.

Tourmaline.—Since this mineral is not an uncommon constituent of many pegmatites, it is sometimes found in kaolins derived from them, the writer having occasionally noted some good-sized crystals in the clay.

The mineral has also been observed in small grains in many other clays of both residual and transported character.

Somers [5] found on making a comparison of raw tourmaline-bearing clays, with fired ones, that the tourmaline seemed to have disappeared above 1150° C. Bayley states that it weathers to ferriferous minerals.[6]

Glauconite, a hydrous silicate of potash and iron, is a common ingredient of some clays. Its composition is often somewhat variable, and it may contain other ingredients as impurities. Thus a sample from New Jersey analyzed: [7] Silica 50.70 per cent, alumina 8.03 per cent, iron oxide 22.50 per cent, magnesia 2.16 per cent, lime 1.11 per cent, potash 5.80 per cent, soda 0.75 per cent, water 8.95 per cent. It is an easily fusible mineral, and hence a high percentage of it is not desired in a clay. It is found in the Clay Marl formations of the New Jersey

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[1] Trans. Amer. Ceram. Soc., XIII, p. 689, 1911.

[2] Hofman and Mostowitch, Chem. Age., II, p. 194, 1920.

[3] U. S. Geol. Surv., Bull. 708, p. 299, 1921.

[4] Teall, J. J. H., Min. Mag., III, p. 201; Ladd, G. E., Amer. Geol., XXIII, p. 240, 1899.

[5] U. S. Geol. Surv., Bull. 708, p. 300, 1921.

[6] Econ. Geol., XV, p. 236, 1920.

[7] N. J. Geol. Surv., Fin. Rept., VI, p. 46, 1904.

Cretaceous,[1] and in the Eocene formations of Maryland [2] and other coastal plain states.

Hornblende and Garnet.—These are both silicate minerals of complex composition, which are probably present in many impure clays, but their grains are rarely larger than microscopic size. Both are easily fusible, and weather readily on account of the iron oxide in them, and therefore impart a deep-red color to clays formed from rocks in which they are a prominent constituent.

Garnet in fair-sized grains has been noted by the writer in some of the North Carolina kaolins.

Vanadates, though not common in clays, may cause discoloration. In Germany they have been found in clays associated with the lignites, and also in some fire-clays,[3] and they occur in the clays of other countries. Clays containing soluble vanadates, if not burned at a sufficiently high temperature, will show on the surface of the ware a green discoloration which, though it can be washed off with water, will continue to return as long as any of the salt is left in the brick. Vanadates may be rendered insoluble by burning the clay to a point of vitrification.[4]

Wavellite.—This mineral, which has the formula $Al_6(OH)_6(PO_4)_4 + 9H_2O$, has been found in the white clay associated with manganese and iron ores on the northern slope of South Mountain, near Mt. Holly Springs, Pa.[5] The wavellite which occurs in aggregates of white nodules, appears to be limited to a streak of the residual clay 40 to 50 feet wide.

Its occurrence has also been mentioned by Hopkins from North Valley Hill in Chester County, Pa.[6]

Manganese oxides.—These occur in many clays in small amounts, and when determined are found to rarely exceed 1 per cent. In some residual clays the manganese has been sufficiently concentrated to be worth collecting.

Vivianite ($Fe_2P_2O_8 + 8H_2O$ = FeO 43 per cent, P_2O_5 28.3 per cent, H_2O 28.7 per cent) has not been described as a common constituent of clay. It has been noted in certain Pleistocene clays of Maryland,[7] in which it occurs as small blue spots. The mineral has also been described as occurring in the form of bluish black stains, of spherical to elliptical form on a light gray fire-clay at Claybank, Saskatchewan. The stains show a banded structure.[1] It is not known what effect large quantities of it might have on the clay.

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[1] Ibid., p. 151.

[2] Md. Geol. Surv., Eocene, p. 52, 1901.

[3] Seger, Ges. Schrift, p. 301; also Tonindus.-Zeit., 1877, No. 46, p. 53.

[4] Ibid.

[5] G. W. Stose, U. S. Geol. Surv., Bull. 315, p. 474, 1907.

[6] Ann. Rept. Pa. State Coll., 1889–1900, Appen. 3, p. 13.

[7] Md. Geol. Surv., IV, p. 228, 1902.

Rare elements.—Even such rare elements as cerium, yttrium, and beryllium oxides have been determined in some clays.[2] Another writer mentions molybdenum, copper and cobalt.[3]

Topaz.—This mineral is sometimes found in pegmatites, and so might be present in kaolin resulting from their decomposition. C. E. Miller has informed the author that he has found large quantities of it in the sandy residue obtained from the washing of some North Carolina kaolins.

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[1] Stansfield, J., Geol. Mag., LIX, p. 356, 1922.

[2] J. R. Strohecker, Jour. prakt. Chem. (2), XXXIII, p. 132; Abs. Jour. Chem. Soc., L, p. 314, 1886.

[3] Deutsch. Töpf. u. Zieg. Zeit., 1880, p. 367, and 1881, p. 387.

CHAPTER III

CHEMICAL PROPERTIES OF CLAY

CHEMICAL ANALYSIS OF CLAY

THERE are two methods of quantitatively analyzing clays. One of these is termed the ultimate analysis, the other is known as the rational analysis.

The ultimate analysis.—In this method of analysis, which is the one usually employed, the various ingredients of a clay are considered to exist as oxides, although they may really be present in much more complex forms. Thus, for example, calcium carbonate ($CaCO_3$), if it were present, is not expressed as such, but instead it is considered as broken up into carbon dioxide (CO_2) and lime (CaO), with the percentage of each given separately. The sum of these two percentages would, however, be equal to the amount of lime carbonate present.

The ultimate analysis of a clay might be expressed as follows:

		Silica	(SiO_2)
		Alumina	(Al_2O_3)
Fluxing impurities.		Ferric oxide	(Fe_2O_3)
		Ferrous oxide	(FeO)
		Lime	(CaO)
		Magnesia	(MgO)
	Alkalies.	Potash	(K_2O)
		Soda	(Na_2O)
		Titanic oxide	(TiO_2)
		Sulphur trioxide	(SO_3)
		Carbon dioxide	(CO_2)
		Organic matter.	
		Water	(H_2O)

In most analyses the first eight of these, excepting the fourth, and the last one are usually determined. The percentage of carbon dioxide is small, except in very calcareous clays, and therefore commonly remains undetermined. Titanic oxide is rarely looked for, except in fire-clays, and even here its presence is frequently neglected. Since the sulphur trioxide, carbon dioxide, and water are volatile at a red heat, they are often determined collectively and expressed as "*loss on ignition.*" If carbonaceous matter, such as lignite, is present, this also will burn off at redness. To separate these four, special methods are necessary, but they are rarely applied, and in fact are not very necessary except in calcareous clays or highly carbonaceous ones. The loss on ignition in the majority of *dry*[1] clays is chiefly chemically combined water. The ferric oxide, lime, magnesia, potash, and soda are termed the fluxing impurities, and their effects are discussed under the head of Iron, Lime, Magnesia, etc., and also under Fusibility in Chapter V.

All clays contain a small but variable amount of moisture in their pores, which can be driven off at 100° C. (212° F.). In order, therefore, to obtain results that can be easily compared, it is desirable to make the analysis on a moisture-free sample which has been previously dried in a hot-air bath. This is unfortunately not universally done.

Interpretation of ultimate analysis.—Much has been said for and against the usefulness of the ultimate analysis of a clay to be used for the manufacture of burned clay wares,[2] but whatever the predominating opinion, ultimate analyses are still made. Many ceramists see little need for the chemical analysis except in special cases, while other persons, not all ceramists, attempt to make all sorts of interpretations from it. One defect of the ultimate analysis is that it gives little information regarding the physical properties of the clay, and these are all important. It might also be reasonably argued that even in the case of those physical properties which are shown by the analysis, their determination is often more easily accomplished by other and simpler tests. The ultimate analysis often lacks also some of the value which it might possess, through neglect to determine separately such substances as titanium oxide, sulphur trioxide, carbon and ferrous iron.

Attempting to regard the matter from a fair and conservative standpoint, it would seem that the following data are obtainable from the ultimate composition, remembering, however, that there may be exceptions to every case, which do not necessarily render the conclusions worthless.

1. The purity of the clay, showing the proportions of silica, alumina, combined water and fluxing impurities present. High grade clays often

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[1] This means dried at 100° C. until their weight is constant. See under Moisture.

[2] Clay for Portland cement is not considered, of course, in this discussion, as every one admits the necessity of chemically analyzing such material.

show a percentage of silica, alumina and chemically combined water approaching quite closely to kaolinite.[1] (See analyses I and II below.)

2. The approximate refractoriness of a clay; for other things being equal, a clay with high total fluxes, is commonly less refractory than one with low total fluxes. In this connection it is to be remembered that texture, irregularity of distribution of the constituents, and condition of kiln atmosphere are among conditions affecting the result.

3. The color to which the clay burns. This must be judged with caution. Assuming the constituents to be evenly distributed, then a clay with 1 per cent or less of ferric oxide is likely to burn pure white, but at high temperatures titanium if present produces discoloration. One with 2–3 per cent of ferric oxide is likely to burn buff; one with several per cent or more of ferric oxide will usually burn red if there is no excess of lime or alumina.[2] It should be remembered that condition of the kiln atmosphere, texture of the clay, and sulphur in the fire-gas may all affect the results.

4. The quantity of chemically combined water. Clays with a large amount sometimes show a high shrinkage, but there are many exceptions to this.

5. Excess of silica. A high percentage of silica (80–90 per cent) may indicate a sandy clay, and possibly one of low shrinkage, but does not necessarily point to a very lean one. High silica in a fire-clay usually shows moderate refractoriness provided it is evenly distributed.

6. Organic matter. This should be determined, as it causes trouble in burning if present to the extent of several per cent,[3] requiring thorough oxidation in firing before the clay is allowed to pass to the vitrification stage.

7. Sulphur trioxide. Since this may be the cause of swelling in improperly burned wares, and also indicate the presence of soluble sulphates, it should always be determined.[4]

8. The presence of several per cent of lime and carbon dioxide shows the clay to be of calcareous character, and not only often of buff-burning character, but with a narrow margin between vitrification and viscosity.

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[1] Exceptions would be those containing other hydrous silicates, such as halloysite or aluminum hydrates.

[2] See Iron, Lime, Alumina.

[3] See Carbon, Iron Oxide, Changes in Burning.

[4] See Sulphur; Sulphates.

9. Titanium dioxide should be determined, especially in fire-clays, for, as has been shown by the author,[1] a small quantity may reduce the fusion point of fire-clay several cones.

It might seem from the above, that the ultimate analysis yields us much, and yet it leaves us practically in the dark as to the plasticity, air and fire shrinkage, density and hardness of burning, transverse strength, or other physical properties, and nothing very definite as to the mineral composition.

Two clays which show marked resemblance in their chemical composition may show a wide divergence in their physical properties.

As an illustration of this we have the two following clays from Harrisburg, Tex., which form different beds in the same bank. Their characters are given in parallel columns.

Silica (SiO_2)	80.39	80.84
Alumina (Al_2O_3)	9.82	8.09
Ferric oxide (Fe_2O_3)	2.88	2.25
Lime (CaO)	.42	1.44
Magnesia (MgO)	.45	.26
Soda (Na_2O)	.19	.10
Potash (K_2O)	Tr.	Tr.
Titanic oxide (TiO_2)	.35	.78
Water (H_2O)	3.11	6.00
	97.61	99.76
Water required for mixing, per cent	18.7	19.8
Average tensile strength, pounds per square inch	188	275
Air shrinkage, linear, per cent	4.8	8.6
Plasticity	Fair	High
Drying	No cracking	Cracks
Absorption Cone 5, per cent	15.64	8.19
Steelhard	Cone 9	Cone 5

A more interesting contrast could hardly be desired, and it forms no exception.

Variation in chemical composition of clays.—The variation in the ultimate composition of clays is well brought out by the following analyses:

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[1] See Titanium.

ANALYSES SHOWING VARIATION IN COMPOSITION OF CLAYS

	I	II	III	IV	V	VI	VII	VIII	IX	X
Silica (SiO_2)	46.3	45.70	57.62	59.92	68.62	82.45	54.64	38.07	90.00	47.92
Alumina (Al_2O_3)	39.8	40.61	24.00	27.56	14.98	10.92	14.62	9.46	4.60	14.40
Ferric oxide (Fe_2O_3)	......	1.39	1.9	1.03	4.16	1.08	5.69	2.70	1.44	3.60
Ferrous oxide (FeO)	......	......	1.2							
Lime (CaO)	......	.45	.7	Tr.	1.48	.22	5.16	15.84	.10	12.30
Magnesia (MgO)	......	.09	.3	Tr.	1.09	.96	2.90	8.50	.10	1.08
Potash (K_2O)	......	2.82	.5	.64	3.36	.....	5.89	2.76	Tr.	1.20
Soda (Na_2O)	......	......	.2							1.50
Titanic oxide (TiO_2)	......	......	.....	.....	......	1.00	.....	......	.70	1.22
Water (H_2O)	13.9	8.98	10.5	9.70	3.55	2.4	3.74	2.49	3.04	4.85
Moisture	......	.35	2.7	1.12	2.78	.....	.85			
Carbon dioxide (CO_2)	......	......	.....	.....	......	.....	4.80	20.46	.....	9.50
Sulphur trioxide (SO_3)	......	......	.35	.....	......	.....	.....	......	.....	1.44
Organic matter	......	......	.....	.....	......	.....	.....	......	.....	1.34
Manganous oxide (MnO)	......	......	.....	.....	.64	.....	.76			
Total	100.00	100.39	99.97	99.97	100.66	99.03	99.05	100.28	99.98	100.35

I. Kaolinite.
II. Kaolin, Webster, N. Ca.
III. Plastic fire-clay, St. Louis, Mo.
IV. Flint fire-clay, Salinesville, O.
V. Loess-clay, Guthrie Centre, Ia.
VI. Rusk, Cherokee County, Tex.
VII. Brick shale, Mason City, Ia.
VIII. Calcareous clay, Milwaukee, Wis.
IX. Sandy brick-clay, Colmesneil, Tex.
X. Blue shale-clay, Ferris, Tex.

Variations in the same deposit.—Similar differences may not infrequently be shown by the different layers of any one bank, as the following analyses indicate:

ANALYSES SHOWING VARIATIONS IN THE SAME DEPOSIT

	I	II	III
Silica (SiO_2)	59.10	51.5	56.2
Alumina (Al_2O_3)	28.84	17.6	23.7
Ferric oxide (Fe_2O_3)	1.00	16.6	1.5
Lime (CaO)	.70	1.00	.6
Magnesia (MgO)	None	1.1	1.5
Potash (K_2O)	Trace	1.5	1.4
Soda (Na_2O)	Trace	Tr.	2.2
Titanium oxide (TiO_2)	.87	1.6	1.6
Water (H_2O)	9.30	7.7	11.1
	99.81	98.6	99.8

Rational analysis.—This method has for its object the determination of the different mineral compounds present in a clay, and several methods have been suggested for making it,[1] but it must be admitted that most if not all of them are unsatisfactory.

The rational analysis when first introduced was applied only to high-grade clays, which were supposed to be made up of " clay substance " (having the composition of kaolinite), quartz, and feldspar.

The object of making it was that, knowing the percentages of these three constituents of a kaolin, one could in substituting another kaolin of different rational composition for it, make allowance for this difference in the proportions of flint and feldspar that were added to the mixture.

The methods for making the rational analysis were derived with a view to separating these components by treatment with acids and alkali hydroxides.

The difficulty with any of these methods is that in the first place, many clays are not so simple in their constitution, and secondly, as pointed out by Ries, Washington and others,[2] the different constituents show a variable resistance to the chemical reagents, while other variations may be due to strength of reagents, temperature, time, size of grains, etc.

H. S. Washington in criticizing these methods states that they are " scarcely susceptible of yielding satisfactory duplicate results except by chance, and even satisfactory duplication of results cannot be regarded as evidence, still less of proof of their correctness, when the methods are seriously faulty.[3]

There is much truth in this observation and the faulty nature of this method of analysis, is now widely recognized.

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[1] Manual of Ceramic Calculations, Amer. Ceram. Soc., Binns, C. F., Zimmer, W. H., and Orton, E., Jr., Trans. Amer. Ceram. Soc., II, p. 221, 1900; Bollenbach, H., Sprechsaal, 1908, No. 25, p. 340, and No. 26, p. 351; Dorfner, J., Sprechsaal, XLVIII, No. 24, 1915; Heath, A., and Green, A. T., Handbook of Ceramic Calculations, p. 132, 1922; Jackson and Rich, Jour. Soc. Chem. Ind., XIX, p. 1087, 1900; Langenbeck, K., Chemistry of Pottery, p. 8, 1895; Mellor, J. W., London Jour. Gas. Lighting, CIII, p. 459, 1908; Mellor, J. W., Quantitative analysis, p. 658, 1913; Purdy, R. C., Trans. Amer. Ceram. Soc., XVI, p. 359, 1912; Ricke, R., Ber. deut. keram. Ges., III, pp. 24–30, 1922; Seger, H., Collected Writings, I, p. 50, 1902; Stremme, H., Ber. der Tech.-Wiss. Abt. des Verb. ker. Gew. v. Deutschland, II, p. 15, 1912; Watts, A. S., U. S. Bur. Mines, Bull. 53, p. 38, 1913; Backe, H., Keram. Runds., XXXIV, p. 20, 1926; Archbutt, L., Jour. Soc. Chem. Ind., XI, p. 215, 1892.

[2] Ries, Trans. Amer. Ceram. Soc., IX, p. 772, 1907; Washington, Jour. Amer. Ceram. Soc., I, p. 405, 1918; Langenbeck, Chemistry of Pottery, p. 3–12; Seger, Collected Writings, I, p. 53 and 543; Jackson and Rich, Jour. Soc. Chem. Ind., Dec. 31, 1900, p. 1087; Galpin, S. L., Trans. Amer. Ceram. Soc., XIV, p. 334, 1912; Zschokke, Baumaterialienkunde, VII, p. 165, 1902; Tilley, G. S., and Sullivan, J. D., Jour. Amer. Ceram. Soc., VIII, p. 379, 1924.

[3] Jour. Amer. Ceram. Soc., I, p. 405, 1918.

However, in former years, before the mineralogy of clays, and the varying results produced by reagents under different conditions were understood, the rational analysis was widely used, and many sincerely believed in its value.

A second possible method of determining the rational composition of a clay is by calculation from the ultimate analysis.

This has been discussed in some detail by Washington,[1] who used the method employed by petrographers to figure out from the chemical analysis the mineral composition of rocks made up of silicate minerals.

In this calculation the potash is assigned to orthoclase feldspar, any soda present to albite, and lime usually to anorthite. The remainder of the alumina is then assigned to kaolinite, while any silica left over is figured as quartz. Iron oxide is calculated as limonite. There is given below an ultimate analysis of a crude kaolin from Webster, N. C., and its rational analysis as made by one of the conventional methods, as well as the rational analysis calculated by Washington.

Ultimate analysis		Rational analysis made		Rational analysis calculated *		
SiO_2	62.40	Clay substance	66.33	Kaolinite		61.92
Al_2O_3	26.51	Feldspar	18.91	Orthoclase	5.56	
Fe_2O_3	1.14	Quartz	15.61	Anorthite	2.74	
CaO	.57					
MgO	.01		100.85	Total feldspar		8.30
Alkalies	.98			Quartz		28.80
Ignition loss	8.80			Limonite		1.26
	99.91					100.28

*Alkalies calculated as K_2O.

It will be seen that there is an appreciable difference between the results of the two methods, and while one might argue that the laboratory method is likely to be in error, because of influencing factors noted above, the method by calculation is equally open to criticism in assuming that kaolinite, feldspar and quartz are the dominant minerals. Petrographic study of clays, especially high-grade ones, the type to which the rational analysis has usually been applied, indicates that feldspar is a relatively rare constituent, while muscovite or hydromicas may be very prominent.

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[1] Jour. Amer. Ceram. Soc., I, p. 405, 1918. See also Buckley, E. R., Wis. Geol. and Nat. Hist. Surv., Bull. 7, Pt. I, p. 267, 1901, and Binns, C. F., Trans. Amer. Ceram. Soc., VIII, p. 198, 1906.

Furthermore there is no knowing how much of certain substances like the alkaline earths and alkalies may be present in adsorbed form, rather than as constituents of silicate minerals.

Thus Binns [1] has shown that all of the alkali present is not necessarily an ingredient of feldspar, but may be free alkali held in the clay by adsorption, and removable by dilute hydrochloric acid. Experiments made by him showed that the less free alkali a clay contains the more it will absorb when allowed to do so. The amount of free alkali found in a series of clays examined ranged from .079 per cent to .22 per cent, while the quantity of potassium carbonate absorbed varied from .087 per cent to .409 per cent (Fig. 35).

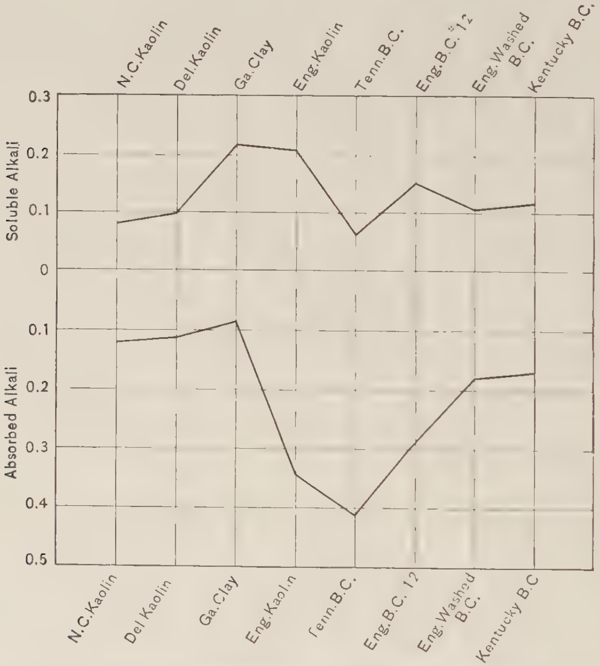

FIG. 35.—Diagram showing percentage of soluble and absorbed salts in clays. (After Binns, Trans. Amer. Ceram. Soc., VIII.)

All considered the method of calculating the rational composition from the ultimate analysis is not much better than the original one.

Zschokke [2] has suggested a combination mechanical and rational analysis, but it is of doubtful superiority to the others already described.

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[1] Trans. Amer. Ceram. Soc., VIII, p. 198.

[2] Baumaterialienkunde, VII, p. 165, 1902.

Even if we have a fairly accurate estimate of the mineralogic composition of the clay, it still fails to give us much information regarding many of its properties, since much depends upon the size of the different mineral grains, and quantity of colloidal matter.

The following methods for making the ultimate and also the rational analysis of clays have been recommended by the Committee on Standards, of the American Ceramic Society.

Method of Ultimate Analysis

Moisture.—To determine moisture, heat approximately 1 gram of the sample at a temperature not under 105 or over 110° C., to constant weight.

Ignition Loss.—To determine loss on ignition, heat about 1 gram of he sample over a blast lamp or in an electric furnace at 900 to 1000° C., o constant weight. Ignition loss may be determined in the sample rom which the moisture has been removed. The percentage of ignition loss is calculated to a moisture-free basis.

Silica.—To determine silica, weigh out approximately 0.5 gram of he sample and mix with 5 grams of sodium carbonate. Put a little odium carbonate in the bottom of the crucible before introducing the mixture, and then cover the mixture with a little more sodium carbonate. Fuse over a Meker burner or blast lamp until complete solution is obtained. Cool the fusion and as it solidifies, rotate the crucible to pread the mass up the side walls. Dissolve the fusion in about 100 c.c. of water in a platinum or porcelain evaporating dish. Add about 20 c.c. of concentrated hydrochloric acid, introducing it slowly by means of a pipette, keeping the dish covered with a watch glass. Evaporate o dryness and heat until the fumes of hydrochloric acid are gone. Add about 5 c.c. of concentrated hydrochloric acid and 30 to 40 c.c. of water. Warm on a water-bath for ten to fifteen minutes and break up he lumps. Decant the clear liquid onto a filter paper and collect the iltrate in a 400-c.c. beaker. Add more hydrochloric acid and water o the evaporating dish, warm again and decant. Repeat this a third time.

Finally transfer the contents of the dish to the filter paper. Wash with cold water until silver nitrate shows no chlorides to be left. Transfer the filtrate to the original evaporating dish, evaporate again to dryness and wash as before. Transfer to a platinum crucible. Ignite carefully over a Bunsen flame until the filter paper is burned off, then blast for about thirty minutes; cool and weigh. Repeat blasting for five minutes, weigh again and repeat until constant weight is obtained.

To the residue in the crucible, add about 5 c.c. of water and fiv drops of sulfuric acid (the latter to prevent the formation of titanium fluoride). Evaporate to dryness. Again moisten with 5 c.c. of wate and five drops of sulfuric acid. Add hydrofluoric acid drop by drop a first, and then slowly until the crucible is almost one-half filled. Warm on a hot plate until almost dry, add 2 or 3 c.c. more of hydrofluoric aci and evaporate to dryness. Heat the crucible to bright redness an then blast for five minutes. Cool and weigh and repeat blasting to constant weight. The loss in weight from the original silica residue represents the actual silica content (SiO_2), except for that part of silica which is later recovered from alumina, etc. The residue from the hydrofluori acid evaporation is left in the crucible and the total precipitate of alumina, etc., is added to this same crucible in which it is ignited an weighed.

Alumina.—To determine alumina, to the filtrate from the silic determination add about 10 c.c. of ammonium chloride and heat t boiling. Then add ammonium hydroxide very slowly and with constant stirring until there is a slight excess. Filter hot and rapidly, an wash four times by decantation with hot solution of ammonium nitrate Carefully wash the precipitate from the filter paper into a beake using hot water. Dissolve the precipitate in hot dilute hydrochlori acid. Repeat the precipitation with ammonium chloride and ammonium hydroxide. Decant four times as before, using hot ammoniu nitrate. Transfer to the filter paper and wash with hot ammoniu nitrate until the washings are free from chlorides when tested by silve nitrate. Evaporate the filtrate nearly to dryness, add a little ammonium hydroxide and continue the evaporation. Keep the solutio alkaline to coagulate any iron and aluminum hydroxides. Transfe the precipitate to a filter paper and wash thoroughly. Transfer th moist filter paper to the platinum crucible containing the residue from th silica. Burn off the filter paper and blast the precipitate. Cool in desiccator and then moisten with one drop of nitric acid and hea gently until all fumes are gone. Blast again and weigh. Repeat blasting and weighing to a constant weight.

Iron Oxide.—To determine iron oxide, fuse the ignited alumina precipitate with about six times its weight of potassium pyrosulfate or potassium bisulfate. Avoid sputtering. Heat carefully to redness and continu heating until the residue is all dissolved. Cool. Dissolve in warn water, add about 10 c.c. of dilute sulfuric acid (1 : 5). Evaporate t a small volume. Then heat to a higher temperature until copiou fumes of sulfuric acid are evolved. Sufficient sulfuric acid should b present to form a pasty mass when cooled. Evaporate to dryness, filte off, wash, ignite and weigh the silica as before and evaporate with hydrofluoric acid as before. The loss in weight is extra silica to be added to the original silica determination and subtracted from the alumina. Fuse the residue with a little potassium pyrosulfate or potassium bisulfate, and add the solution of this cake to the main solution. Transfer the total filtrate to a 250-c.c. graduated flask and dilute to 250 c.c. mixing thoroughly. Draw off 50 c.c. of this solution and reserve for titania determination. Pass the remaining 200 c.c. through a Jones reductor, or otherwise reduce the solution with pure zinc and sulfuric acid. To the solution add 3 c.c. of 10 per cent copper sulfate solution and titrate with standard potassium-permanganate solution (1 c.c. equivalent to 0.0001 gram Fe_2O_3), until a faint pink tinge is seen. If Jones reductor or similar apparatus is used, subtract the potassium permanganate equivalent, which has previously been determined on blank samples run through the apparatus. From the result, calculate the iron as iron oxide (Fe_2O_3).

Titania.—To determine titania, place in a small Nessler tube the 50 c.c. of filtrate previously set aside for titania determination, and fill the tube up to the graduation mark. Add 1 c.c. of hydrogen peroxide and shake well. The color of this solution is now compared in any standard color comparator with the color of a known standard solution, preferably of such strength that 1 c.c. equals 0.0001 gram of titanium dioxide (TiO_2). To make the comparison, put 10 c.c. of this standard solution into a second small Nessler tube and dilute with water from a burette until the color is matched. Note the amount of water added and calculate the percentage of titanium dioxide in the sample.

Lime.—To determine lime, evaporate the filtrate from the alumina precipitation to about 250 c.c. While still boiling add about 5 c.c. of acetic acid. Meanwhile, dissolve about 1 gram of oxalic acid in a little hot water and add to the solution. In about five minutes add a slight excess of ammonium hydroxide and boil until precipitation is complete. Cool thoroughly and filter. Wash three times by decantation with dilute ammonium hydroxide (1 : 10) or a 1 per cent solution of ammonium oxalate. Dissolve the precipitate by adding about 50 c.c. of dilute nitric acid (1 : 5). Again add a slight excess of ammonium hydroxide and a few drops of oxalic-acid solution. Boil well and let stand a couple of hours to cool. Filter and wash as before. Transfer the precipitate to a platinum crucible, carefully burn off the paper and gnite over a blast lamp for about ten minutes. Cool and weigh quickly. Repeat the blasting to constant weight. The increase in weight of crucible is calcium oxide.

Magnesia.—To determine magnesia, add to the filter from lime precipitation about 2 grams of sodium-ammonium-phosphate dissolved in 15 c.c. of water. Stir vigorously and while stirring add drop by drop about one-third of the volume of the solution of ammonium hydroxide. Let stand twelve to twenty-four hours. Filter and wash the precipitate with dilute ammonium hydroxide (1 : 10). The filtrate is discarded. Wash the precipitate until the washings show no discoloration when tested with silver nitrate. Redissolve the precipitate in warm dilute nitric acid (1 : 5) using about 50 c.c., and collect in a beaker. Precipitate and wash as before. Collect the precipitate on a Gooch asbestos crucible. Dry slowly and then heat over a Meker burner for about ten minutes; cool and weigh. Reignite to constant weight.

Alkalies.—To determine alkalies, the J. Lawrence Smith method shall be used. Weigh out about 0.5 gram of the sample and mix well with 0.5 gram ammonium chloride and 3 grams calcium carbonate. Transfer to a platinum crucible, placing about 0.5 gram calcium carbonate in the bottom of the crucible and a similar amount over the top of the mixture. Heat gently over a low flame for about fifteen minutes to volatilize ammonium chloride. Then raise the temperature until the lower three-quarters of the crucible is dull red. Hold this temperature for about one hour. Cool, take up with about 50 c.c. of water and heat over a water bath, adding water to replace that lost by evaporation. Break up any lumps with a small pestle. Decant the clear liquid through a filter paper and wash four times by decantation. Then transfer the residue to the filter. Wash until silver nitrate shows only a very faint turbidity. To the filtrate add ammonium hydroxide and ammonium carbonate and heat to boiling. Filter and again digest the precipitate with ammonium hydroxide and ammonium carbonate. Filter and allow the filtrate to collect with the previous filtrate, then evaporate to dryness in a platinum or porcelain dish. Remove ammonium salts by gentle ignition in a moving flame. Treat with water and remove the last trace of lime by adding ammonium oxalate to the boiling solution and let stand overnight. Filter, evaporate to dryness, ignite gently and allow to cool. Then moisten the residue with hydrochloric acid, evaporate again to dryness, ignite gently and weigh. The increase in weight is potassium chloride plus sodium chloride. Dissolve in water. Ignite and weigh any insoluble residue, deducting this from the mixed chlorides.

Dilute the solution of the mixed chlorides and add hydrocholoroplatinic acid in amount equal to 0.3 c.c. more than would be necessary if all chlorides were present as sodium chloride. Evaporate to a syrupy consistency. Cool and treat with a few cubic centimeters of 80 per cent ethyl alcohol. Stir and decant through a weighed Gooch crucible.

Treat again with 80 per cent alcohol and decant. Repeat washing and decantation until the alcohol leaving the Gooch crucible is colorless and the precipitate appears golden yellow, not orange. Transfer the precipitate to the Gooch crucible, wash with 80 per cent alcohol about six times and dry at 130° C. to constant weight.

The oxides are calculated as follows:

Weight of potassium chloroplatinate $\times$ 0.3068 = potassium chloride.

Weight of potassium chloroplatinate $\times$ 0.1040 = potassium oxide (K_2O).

Total chlorides − potassium chloride = sodium chloride.

Sodium chloride $\times$ 0.5305 = sodium oxide (Na_2O).

TENTATIVE METHOD FOR RATIONAL ANALYSIS

Preface.—It will be understood that the rational analysis as herein outlined is applicable chiefly to the relatively pure types of clays and that, in general, its applicability decreases with increasing impurity of the clay.

Precautions.—Since it is a well-established fact that the treatments during rational analysis attack the different feldspars, micas, and many other minerals to a greater or less degree, it is very important that the details of procedure be followed carefully, especially as to concentration of the solutions and the time of treatments. For discussion of various details frequent reference should be made to Mellor, "Treatise on Ceramic Industries," Vol. II, and to Bollenback's articles in "Sprechsaal," 1908, p. 340–3, 351–4, a condensed translation of which is given in Bulletin No. 53, Bureau of Mines, by Watts.

Direct Method.—Weigh out 5 grams of the powdered clay sample previously dried at 110° C. (or a moisture test may be run separately and the rational analysis results calculated to a moisture-free basis). Place the sample in a porcelain dish of about 1000 c.c. capacity and add 100 c.c. of water. Heat to boiling and boil for about five minutes to accomplish a thorough disintegration of clay lumps. If necessary add a drop or two of NH_4OH to help disintegrate the mass. Any water lost during boiling should be replaced.

Add 100 c.c. of H_2SO_4 (1 : 1 mixture) and cover with a watch glass. If the clay contains organic matter as shown by dark coloration add a few drops of concentrated HNO_3. Heat gently to boiling and continue heating for about one hour until all water is evaporated and copious fumes of H_2SO_4 appear.

Allow to cool, add water until the dish is nearly filled and mix thoroughly. Wash off the stirring-rod and cover glass. Let the dish stand quietly for about four hours until thoroughly settled, then decant into a large beaker using care to permit no solid matter to be transferred.

Add to the residue in the dish about 300 c.c. of a mixture made by dissolving 100 grams of Na_2CO_3 and 10 grams of NaOH in water making the solution up to 1000 c.c. Heat the mixture to boiling and stir frequently. Again wash off rod and watch glass and set the solution aside for about two hours. The supernatant solution should be clear, any turbidity indicating lack of complete decomposition of the clay. Again decant off the clear solution. Stir up the residue with about 400 c.c. of concentrated HCl. Heat the mixture to boiling and boil for about five minutes to dissolve iron hydroxide, etc. Add about 200 c.c. more of water, stir vigorously and then let stand for about five hours.

Decant off the clear liquid and repeat both alkali and the acid treatments as outlined above.

After the final decantation following acid treatment stir up the remaining mass with about 200 c.c. of water and wash the residue on to a dense filter paper, using dilute HCl (1 : 2 mixture) to accomplish the transfer. On the filter paper wash twice with the dilute HCl and three times with water. Transfer the residue in the filter paper to a weighed platinum crucible, ignite over a medium blast flame or Meker burner. The ignited residue is feldspar plus quartz.

Fuse this main residue (of feldspar plus quartz) with about five times its weight of sodium carbonate in a platinum crucible. Heat carefully over a Bunsen flame and increase the heating until complete fusion has taken place. Care must be used to avoid spattering. After fusion is complete, blast for a few minutes. Cool and as the fusion becomes stiff, tilt and rotate the crucible so as to distribute the mass up the sides of the crucible. Place the crucible in a beaker, cover with water and add about 10 c.c. of hydrochloric acid. Digest until the mass is completely disintegrated.

Now transfer all of the residue and solution to an evaporating-dish and evaporate to dryness. Redissolve in concentrated hydrochloric acid, heat for about fifteen minutes, dilute with water and again evaporate to dryness.

Soak the residue in hydrochloric acid for about fifteen minutes, dilute with water, heat for about fifteen minutes more on a water-bath, dilute again and filter. In filtering, decant off the clear liquid and finally transfer the silica to the filter paper by washing out with cold, dilute hydrochloric acid.

Wash thoroughly with hot water. Transfer the filter paper to a platinum crucible, ignite gently and finally blast for about twenty minutes. Cool and weigh.

Calculations.—The main residue (of feldspar plus quartz) minus the silica just determined equals potash plus alumina in the feldspar. This difference (potash plus alumina) multiplied by 2.837 equals the feldspar. The main residue minus the feldspar equals the quartz. The original sample minus the sum of feldspar and quartz (the main residue) equals clay substance. Since 0.5 gram was taken of the sample, all figures must be multiplied by 2 to give percentages.

Other Constituents.—If it is required to include other constituents such as soluble salts, carbon in form of carbonates, silicic acid, and so forth, these should be determined on a separate sample and the corresponding amounts, reduced to a moisture-free basis, subtracted from the total clay substance.

Method of Calculation from Ultimate Analysis.—If it is desired to express the ultimate analysis in terms of rational analysis the following methods of calculation shall be followed:

Na_2O multiplied by 5.60 = SiO_2 in Na-feldspar.
K_2O multiplied by 3.83 = SiO_2 in K-feldspar.
Na_2O multiplied by 1.65 = Al_2O_3 in Na-feldspar.
K_2O multiplied by 1.09 = Al_2O_3 in K-feldspar.

Total Al_2O_3 minus Al_2O_3 in feldspar = Al_2O_3 in clay substance.

Al_2O_3 in clay substance multiplied by 1.18 = SiO_2 in clay substance.

SiO_2 in quartz = total SiO_2 minus (SiO_2 in clay substance plus SiO_2 in Na- and K-feldspar).

Feldspar = (Na_2O multiplied by 8.45, plus K_2O multiplied by 5.92).

Clay substance = 100 per cent minus (quartz plus feldspar).

MINERAL COMPOUNDS IN CLAY AND THEIR CHEMICAL EFFECTS

All the constituents of clay influence its behavior in one way or another, their effect being often noticeable when only small amounts are present. Their influence can perhaps be best discussed individually.

SILICA [1]

This is present in clay in two different forms, namely, uncombined as silica or quartz, and in silicates. The uncombined silica is usually quartz, but flint, chalcedony, or hydrous silica might be present.

The silicates may be represented by kaolinite or other hydrous aluminum silicates, micas, feldspars, glauconite, hornblende, garnet, etc.

The percentage of both quartz and total silica found in clays varies between wide limits, as can be seen from the following examples. Wheeler gives a mimimum [1] of 5 per cent in the flint-clays, and the sand percentage as 20 to 43 per cent in the St. Louis clays, and 20 to 50 per cent in the loess-clays. Twenty-seven samples of Alabama clays analyzed by the writer contained from 5 to 50 per cent of insoluble residue, mostly quartz.[2] In seventy North Carolina clays [3] the insoluble sand ranged from 15.15 to 70.43 per cent.

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[1] See also description of the minerals quartz, feldspar, kaolinite, and mica above.

The following table [4] gives the variation of total silica in several classes of clays, the results being obtained from several hundred analyses:

Amount of Silica in Clays

Kind of clay	Per cent of total silica		
	Minimum	Maximum	Average
Brick-clays	34.35	90.877	59.27
Pottery-clays	45.06	86.98	45.83
Fire-clays	34.40	96.79	54.304
Kaolins	32.44	81.18	55.44

The free silica or quartz is one of the commonest constituents of clay, and ranges in size from particles sufficiently large to be visible to the eye down to the smallest grains of silt.

With the exception of hydrous aluminum silicates, sericite, and hydrous mica, many of the silica-bearing minerals mentioned above are of rather sandy or silty character, and, therefore, their effect on the plasticity and shrinkage will be similar to that of quartz. In burning the clay, however, the general tendency of all is to affect the shrinkage and also the fusibility of the clay, but their behavior is in the latter respect more individual.

Sand (quartz and silicates) is an important antishrinkage agent, which greatly diminishes the air-shrinkage, plasticity, and tensile strength of clay, its effect in this respect increasing with the coarseness and quantity of the material; clays containing a high percentage of very finely-divided sand (silt) may absorb considerable water in mixing, but show a low air-shrinkage. The brickmaker recognizes the value of the effects mentioned above and adds sand or loam to his clay, and the potter brings about similar results in his mixture by the use of ground-flint.

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[1] Mo. Geol. Surv., Vol. XI, p. 54.

[2] Ala. Geol. Surv., Bull. 6, 1900.

[3] N. C. Geol. Surv., Bull. 13, p. 24, 1898.

[4] Bull. N. Y. State Museum, No. 35, p. 525.

It is thought by some that because of the refractoriness of quartz its addition to any clay will raise its fusion-point, but this is true only of those clays containing a high percentage of common fluxes and silica and which are burned at low temperatures. Its effect on highly aluminous low-flux clays reduces their refractoriness.

In considering the effects of sand in the burning of clays, it must be first stated that the quartz and silicates fuse at different temperatures. A very sandy clay will, therefore, have a low fire-shrinkage as long as none of the sand-grains fuse, but when fusion begins a shrinkage of the mass occurs. We should, therefore, expect a low fire-shrinkage to continue to a higher temperature in a clay whose sand-grains are refractory.

Of the different minerals to be included under sand the glauconite is the most easily fusible, followed by hornblende and garnet, mica (if very fine grained), feldspar, and quartz. The glauconite would, therefore, other things being equal, act as an antishrinkage agent only at low temperatures. Variation in the size of the grain may affect these results, but this point is discussed under Fusibility (Chapter V).

The following tests give interesting data on the effect of quartz on clay.

F. Krage,[1] after experimenting with a series of mixtures made up of a blue clay (fusion point = cone 34), and a red clay (fusion point = cone 6), each mixed with quartz sand grains of different degrees of fineness and burned to cones 08, 6, and 14, drew the following conclusions:

Increased amount of quartz tended to decrease the water of tempering, air- and fire-shrinkage, porosity in soft-burned pieces, crushing and tensile strength; it increased: air drying, porosity in hard-fired pieces, permeability, and ability to stand temperature changes.

Decreased texture of sand, caused: slower drying, lower porosity and permeability, decreased ability to withstand rapid temperature, changes. It increased the tempering water, air- and fire-shrinkage, tensile and crushing strength.

His generalizations that quartz increases the refractoriness do not always hold.

Effect of heat on Silica.—Quartz upon heating passes into a number of both stable and unstable phases as indicated below.[2]

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[1] Der Einfluss des Quarzes von verschiedener Korngrösse auf einen feuerfesten und einen nicht feuerfesten Ton, Tonindus.-Zeit., XXXII, No. 67, p. 934, 1908.

[2] Fenner, C. N., Amer. Jour. Sci., 4th Sci., XXXVI, p. 331, 1913.

Stable phases:

Quartz → Tridymite at 870 ± 10° C.
Tridymite → Cristobalite at 1,470 ± 10° C.

Unstable phases:

α-quartz → β-quartz at 575° C.
β-quartz → α-quartz at 570° C.
α-tridymite → β_1-tridymite at 117° C.
β_1-tridymite → β_2-tridymite at 163° C.

Reversions on cooling not very sharp:

α-cristobalite → β-cristobalite at 274.60° C. to 219.7° C., depending on previous heat treatment.

β-cristobalite → α-cristobalite at 240.5° to 198.1° C., depending on previous heat treatment.

Starting with quartz and a flux, either tridymite or cristobalite may be formed, according to the temperature. Similarly tridymite may be changed into quartz or cristobalite, or cristobalite into quartz or into tridymite.

The change from one to the other is slow, and may go through intermediate phases, until the one of greatest stability is finally formed.

If quartz is heated to high temperatures, in the absence of a flux, it will change to cristobalite even below the tridymite-cristobalite inversion point, but probably not below 1250° C. Tridymite at 1570° C. changes to cristobalite without a flux.

Cristobalite melts at 1710° C., tridymite at 1670° C., and quartz at about 1600° C.

With prolonged heating quartz or cristobalite will change to tridymite without a flux.

The change from one silica mineral to another is slow, but the low temperature transformations involving the α and β forms are rapid and on this account temperature changes cause cristobalite to crack, between 220° C. and 275° C. Tridymite shows the least tendency to crack when exposed to sudden changes of temperature.

Quartz, tridymite and cristobalite can be distinguished by their indices of refraction as follows: Quartz, 1,553–1,544; tridymite, 1,477; cristobalite, 1,484.

The inversion of quartz to the other silica minerals is accompanied by permanent expansion. Thus for quartz to cristobalite the volume increase is 13.6 per cent, while to tridymite it is 16.8 per cent. This accounts for the permanent expansion of silica brick when in use.

The specific gravity of quartz is 2.65, cristobalite, 2.333, and tridymite, 2.27. The density of silica or silica bricks, therefore, decreases on burning.

McDowell[1] in studying a number of silica brick concluded that much of the quartz is transformed into cristobalite on the first burn, and the remainder slowly on repeated burning. The cristobalite gradually turns to tridymite. Tridymite seemed to form first in the finer grained groundmass where lime is present.

Ross[2] states that on burning silica brick with 2 per cent lime, " the silica is transformed first to cristobalite and a small amount of glass composed of silica, lime and other basic fluxing materials." When about 75 per cent of the silica has been converted tridymite appears, but continued burning converts practically all the material to tridymite.

Amorphous silica may change to a crystalline form on heating.

Fenner[3] states that chalcedony at 800° C. in the presence of flux is converted into quartz and tridymite, but that the latter disappears on further heating. He also found that when amorphous silica was heated to 1300 or 1400° C., cristobalite alone was obtained, although tridymite is the stable form for those temperatures. In addition he[4] observed that when amorphous silica was heated to 1030° C. it changed completely to cristobalite after sixty-nine hours' heating, but Houldsworth and Cobb[5] noted the change of amorphous silica to cristobalite, at 700° C., if 5 per cent of soda is present.

Washburn and Navias[6] consider that on heating it is converted partly into isotropic silica glass, and that this later crystallizes forming cristobalite.

A study of the index of refraction and specific gravity of sand, quartz, chalcedony and French flint, when heated to cones 13 and 14, showed that the last two transformed to cristobalite before the first two.[7] The figures follow:

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[1] Trans. Amer. Inst. Min. Engrs., LVII, p. 3, 1918

[2] U. S. Bur. Stand., Tech. Pap., No. 116, p. 66, 1919.

[3] Amer. Jour. Sci., XXXVI, p. 380, 1913.

[4] Amer. Jour. Sci., XXXVI, p. 380, 1913.

[5] Trans. Ceram. Soc. (Eng.), XXI, p. 258, 1921–22.

[6] Jour. Amer. Ceram. Soc., V, p. 565, 1922.

[7] Robson, J. T., Jour. Amer. Ceram. Soc., V, p. 670, 1922; see also Rieke and Endell, Silikat-Z., I, p. 52, 1913; Mellor and Campbell, Trans. Ceram. Soc. (Eng.), XV, p. 77, 1915–16; Washburn and Navias, Jour. Amer. Ceram. Soc., V, p. 565, 1922.

Refractive Index of Different Forms of Silica after Heating

Material	I	II	III
Sand	1.545	1.545	1.509
Quartz	1.545	1.545	1.517
Chalcedony	1.540	1.527	1.495
French flint	1.527	1.487	1.487

I. Index before heating.
II. Index after heating to cone 13 (1390° C).
III. Index after heating to cone 14 (1410° C).

Material	I	II
Sand	2.67	2.49
Quartz	2.66	2.49
Chalcedony	2.66	2.32
Flint	2.58	2.28
Cristobalite	2.32	

I. Specific gravity before firing.
II. Specific gravity at 1430° C.

Searle makes the statement [1] that "in most articles made of fired clay the greater part of the free silica remains as quartz, but partial inversion to cristobalite or tridymite frequently occurs, though these allotropic forms of silica are not readily recognized in fired-clay products."

E. Steinhoff and F. Hartmann [2] claim that by etching and staining methods, it is possible to determine the conversion of the quartz.

Hydrous silica.[3]—From the observations of W. H. Zimmer [4] it would appear that some kaolins carry hydrated silicic acid. In a kaolin of the composition:

Silica (SiO_2)	57.00
Alumina (Al_2O_3)	24.85
Ferric oxide (Fe_2O_3)	.25
Lime (CaO)	.05
Water (H_2O)	17.81

he found that the rational analysis showed only 0.05 per cent not decomposed by sulphuric acid, which would lead one to suppose that the clay was a pure kaolin. The analysis, however, disproved this, and led to the conclusion that there must be free hydrated silicic acid. His experiments with this clay, and with artificial mixtures containing silicic acid, showed that the presence of any important quantity of free hydrated silicic acid in a clay tends:

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[1] Chemistry and Physics of Clays, p. 415.

[2] Stahl u. Eisen, XLV, p. 337, 1925.

[3] In this connection see also Fuller's earth, Chap. VI.

[4] Trans. Amer. Ceram. Soc., III, p. 25, 1901.

1. To produce an increase of translucency over that obtained where the silica used is all quartzitic at equal temperatures; 2, to bring about an improvement in color; 3, to increase the shrinkage both in air and in fire; 4, to produce a lowering of the temperature at which vitrification occurs; 5, a tendency to warp in drying; 6, a tendency to form a hard coating on the surface of the clay or ware, due to the deposition of H_2SiO_3 from water used in making wares plastic.

Pence [1] in commenting on Zimmer's work notes that unless care be taken, there may arise errors in the determination of hydrous silica, and contrary to him, believes that increased colloidal silica causes decreased vitrification, and increased air-shrinkage, but does not produce any uniform effect on the fire-shrinkage.

Alumina

Most of the alumina found in clays is in combination with silica, as a silicate. Free alumina, or that not combined with silica is rare. However, gibbsite and diaspore have been noted in appreciable amounts in some clays from Kentucky and Missouri, respectively. It is also present in quantity in bauxite.

The fusion-point of alumina is 2050° C.,[2] which is considerably above that of kaolinite. The latter, however, is not stable at high temperatures and breaks up into mullite and silica.

The equilibrium diagram of the $Al_2O_3 \cdot SiO_2$ system is shown in Fig. 36.

A high alumina clay will be very refractory, but the proper mixture of alumina and silica, may form a eutectic whose melting-point is as low as cone 26.

Reference is also made to alumina under iron oxide.

Iron Oxide

Sources of iron oxide in clays.—Iron oxide is one of the commonest ingredients of clay, and a number of different mineral species may serve as sources of it, the most important of which are grouped below:

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[1] Trans. Amer. Ceram. Soc., XII, p. 43, 1910.

[2] Kanolt, Jour. Wash. Acad. Sci., III, p. 315, 1913.

Hydrous oxides; oxides: hematite, magnetite; silicates: biotite, glauconite (greensand), hornblende, garnet, etc.; sulphides: pyrite; carbonates: siderite; sulphate: melanterite; phosphate: vivianite.

In some, such as the oxides, the iron is combined only with oxygen, and is better prepared to enter into chemical combination with other elements in the clay when fusion begins. In the case of the sulphides and carbonates, on the contrary, the volatile elements, namely, the sulphur of the pyrite and the carbon dioxide of the siderite, have to be driven off before the iron contained in them is ready to enter into similar union. In the silicates the iron is chemically combined with silica and several bases, forming mixtures of rather complex composition and all of them of low fusibility, particularly the glauconite. Several of these silicates are easily decomposed by the action of the weather, and the iron oxide which they contain combines with water to form hydrated ferric oxide. This is usually in a finely divided condition, so that its coloring action is quite effective.

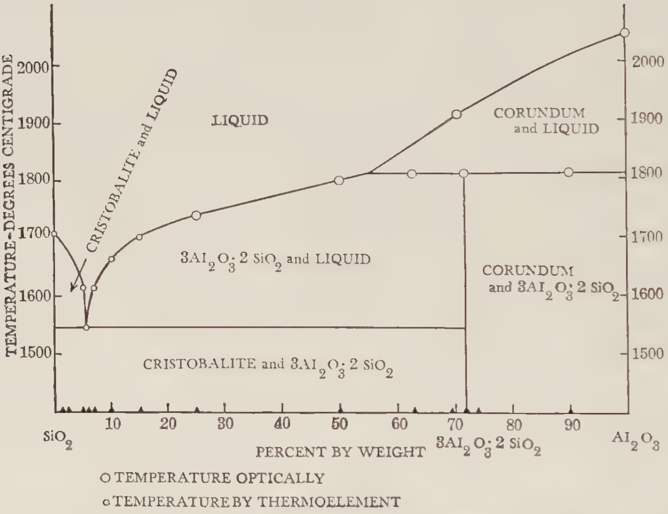

FIG. 36.—Equilibrium diagram of the system $Al_2O_3 \cdot SiO_2$, after Shepherd, Rankin and Wright. (Jour. Amer. Ceram. Soc., VII, 1924.)

The range of ferric oxide, as determined from a number of published clay analyses, is as follows:[1]

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[1] Bull. N. Y. State Museum, No. 35, p. 520.

AMOUNT OF FERRIC OXIDE IN CLAYS *

Kind of clay	I	II	III
Brick-clays..........	0.126	32.12	5.311
Fire-clays...........	0.01	7.24	1.506

I. Minimum.
II. Maximum.
III. Average.

* The percentage of FeO is rarely determined in the ultimate analysis of clay, but it always should be.

Coloring action of iron in unfired clay.—Clays may show a yellow, brown, red, gray or green color due to different iron compounds, these being present as a film on the surface of the grains, or as adsorbed material.

Two clays containing the same amount of iron may show totally different colors, and two materials with different iron content may show the same color.

G. R. McCarthy[1] has brought out that orthoclase acquires an iron stain more readily than quartz, and that aluminum hydrate is a good adsorbent, but that kaolin is a poor one, unless alkali carbonates are present. He has demonstrated that the iron content of clays up to about 5 per cent Fe_2O_3, is a linear function of the alkali content.

The reds, yellows and browns are due to ferric oxides in varying states of hydration. The blue color found in clays, shales, etc., according to the same author [2] are produced by blue iron compounds, of a hydrous ferro-ferric nature, and are not due to organic matter. The iron greens, he considers, are mixtures of iron-blues and iron-yellows, no evidence of the existence of a green compound having been obtained. The iron-purples, other than the chocolate-red of hematite which is often called a purple, he states, appear to be mixtures of iron-blues and iron-reds.

It is, of course, understood that the coloring action of iron is effective only when it is evenly distributed through the clay in a finely divided form.

Coloring action of iron oxide on burned clay.[3]—All of the iron oxides will in burning change to the red or ferric oxide, provided a sufficient supply of oxygen is able to enter the pores of the clay before it is vitrified; if vitrification occurs the iron oxide enters into the formation of silicates of complex composition. The color and depth of shade produced by the iron will, however, depend on: (1) the amount of iron in the clay; (2) the temperature of burning; (3) condition of the iron oxide, (4) the condition of the kiln atmosphere, and (5) degree of fusion

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[1] Jour. Geol., XXXIV, p. 352, 1926.

[2] Amer. Jour. Sci., XII, p. 36, 1926.

[3] See also color of burned clay, Chap. V.

Clay free from iron oxide burns white. If a small quantity, say 1 per cent, is present a slightly yellowish tinge may be imparted to the burned material, but an increase in the iron contents to 2 or 3 per cent often produces a buff product, while 4 or 5 per cent of iron oxide in many cases makes the clay burn red. There seem, however, to be not a few exceptions to the above statements. Thus we find that the white-burning clays carry from a few hundredths per cent to over 1 per cent of iron oxide,[1] the more ferruginous containing more iron than the purer grades of buff-burning clays. Again, among the buff-burning clays we find some with an iron-oxide content of 4 or 5 per cent, an amount equal to that contained in some red-burning ones.

Seger has divided the buff-burning clays into two groups, namely, (1) those of such high iron content as to burn red normally, but which are sufficiently calcareous to enable the lime to destroy the red iron color and form a yellow compound of iron and lime, and (2) those low in iron and high in alumina, which would normally burn pale red, but develop a yellow color due to the formation of an alumina-iron compound. He thus believes that the red coloration of the iron is destroyed by similar causes, but on account of the lime being a stronger or more active base than the alumina it is able to take care of a greater quantity of iron.

Orton [2] has argued against the effect of alumina, claiming that if this were true synthetic mixtures should easily give the buff color which, in his experience, it is not possible to produce. As he states, there is a great uniformity in the color of buff-burning clays, while their iron-alumina ratios fluctuate greatly; some fire-clays containing 40 per cent of alumina and 0.5 per cent iron, and yielding a good buff product, while others with 15 to 20 per cent alumina and 2.5 per cent iron burn to almost exactly the same tint. On the other hand, some clays with about the same alumina and iron content burn red. If Orton is correct it would seem, therefore, as if the cause of this buff-burning quality must be sought for in some other direction.

L. A. Keene [3] presents the somewhat theoretical view that the yellow color of bricks is due to very finely divided Fe_2O_3, and not to any compound of Fe_2O_3 with CaO, or SiO_2, or both. Free Al_2O_3 he seems to think is an important peptizing agent, and CaO is effective in setting free Al_2O_3. If the Fe_2O_3 particles are larger the color is red. If iron is deposited with finely-divided organic matter, the Fe_2O_3 is likely to be precipitated in a finely-divided form, so that the clay may burn buff without CaO or Al_2O_3 being high. This last-named point may be particularly open to question, as some shales or clays high in organic matter may fire to a red color at all temperatures.

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[1] Seger's Collected Writings, Translation, I, p. 109; also Orton, Trans. Amer. Ceram. Soc., V, p. 380.

[2] Trans. Amer. Ceram. Soc., V, p. 389, 1903.

[3] Jour. Phys. Chem., XX, p. 734, 1916.

The evenness of color is apparently closely connected with the physical condition of the iron oxide, that in colloidal form giving a uniformity of shade not obtainable by the admixture of very finely ground material.

If a clay is heated at successively higher temperatures, it is found that, other things being equal, the color usually deepens as the temperature rises. Thus, if a clay containing 4 per cent of iron oxide is burned at a low temperature it will be pale red, and harder firing will be necessary to develop a good brick red, which will pass into a deep red and then reddish purple.

Seger explained the successive shades of red by assuming that the iron oxide increased in density with rising temperature.

The color becomes lighter and brighter as the temperature increases, but when fusion begins the color darkens and changes to a brown.

Some clays retain a good red color even when vitrified, which would seem to indicate that the iron oxide is still free, but on further heating these clays begin to blacken as iron silicates are formed.

Orton also found that a sandy clay retained its red color up to cone 8, while another with more fine clay, reached its maximum color at cone 1.

The brilliancy of the color appears to be influenced by the texture, as the more sandy clays can be heated to a higher temperature, without destruction of the red color, than the more aluminous ones. Alkalies also appear to diminish the brightness of the iron coloration.[1]

Among the oxides of iron two kinds are recognized, known respectively as the ferrous oxide (FeO) and ferric oxide (Fe_2O_3). In both the limonite and hematite the iron is in the ferric form, representing a higher stage of oxidation. In magnetite both ferrous and ferric iron are present, but in siderite the ferrous iron alone occurs. In the ultimate analysis the iron is usually determined as ferric oxide, no effort being made to find out the quantity present in the ferrous form, although if there is any reason to suspect that much of the latter exists it should be determined. Iron passes rather readily from the ferric to the ferrous form. It also oxidizes easily unless carbon and sulphur are present, in which case its oxidation is not possible until these two substances have been oxidized. Indeed they are sometimes supplied with oxygen at the expense of the iron, which may be left in a ferrous, magnetic, or even spongy, metallic condition (Orton) [1]; so if there is a deficiency of oxygen inside of the kiln the iron does not get enough oxygen and the ferrous compound results, but the latter changes rapidly to the ferric condition if sufficient air carrying oxygen is admitted. If, however, the oxidation of the iron does not begin until the clay has become so dense as to prevent free circulation of the air through it, then it may form ferrous silicates, which impart black or dark colors to the clay.[2]

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[1] Ries, N. Y. State Mus., Bull. 35, 515, 1900: Orton, Trans. Amer. Ceram. Soc., V, p. 414, 1903.

There is consequently a necessity for recognizing these two forms of iron oxide because they affect the color of the clay differently. Ferrous oxide alone is said to produce a green color when burned, while ferric oxide alone may give purple or red, and mixtures of the two produce yellow, cherry red, violet, blue, and black.[3]

Seger [4] found that combinations of ferric oxide with silica produced a yellow or red color in the burned clay. We may thus get a variation in the color produced in burning clay, depending on the character of oxidation of the iron or by mixtures of the two oxides.[5]

Moreover, in the burning of ferruginous clays it is usually desirable to get the iron thoroughly oxidized to prevent trouble in the later stages of burning. To accomplish this the iron must be freed of any sulphur or carbon dioxide which may be combined with it, and other volatile or combustible elements in the clay must be driven off, so as to allow the oxidizing gases to enter the clay and unite with any ferrous iron that may be present.

Sulphide of iron (pyrite) loses half its sulphur at a red heat, and the balance will, under oxidizing conditions, not pass off below 925° C.,[6] while siderite or ferrous carbonate loses its carbon dioxide between 400° and 500° C.; magnesium carbonate and calcium carbonate lose their CO_2 at about 500° C.[7] and 800° to 900° C., respectively. Carbonaceous matter or sulphur if present, must also be carefully burned off. If the clay contains much volatile or combustible matter the burning must proceed slowly below 1000° C., in order to remove it and allow the iron to get oxidized while the clay is still porous.

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[1] Third Report Committee on Technical Investigation. Indianapolis, 1908.

[2] See also Tonindus. Zeit., No. 90, p. 1432, 1903; Trans. Ceram. Soc., (Eng.) II, p. 100 (Quoted by Orton, l. c.).

[3] Keramic, p. 256.

[4] Notizblatt, p. 16, 1874.

[5] See "Flashing of Brick," under Burning.

[6] See further under Sulphur.

[7] Brill's work cited under magnesia show that some of the CO_2 may pass off earlier.

After oxidation the clays will show a more brilliant iron color than they do at the end of the dehydration period. They are also harder and show a slight decrease in volume.

If the clay has been improperly oxidized it shows later when vitrification is reached, by the dark ferrous silicate cores in the center of the brick. This may form, however, without the development of any swelling.[1] When swelling does accompany the formation of this black core, it is to be traced to sulphur.

Fine-grained clays are more difficult to oxidize than coarse-grained ones, because of the small size of their pores, and grog is, therefore, added at times to open the grain of the material.

G. C. Matson [2] came to the conclusion that if ferruginous clays are burned to viscosity in an oxidizing atmosphere, that the ferric oxide does not tend to reduce to a ferrous form, as some have believed.

The statements of other observers, however, is to the contrary, for according to LeChatelier,[3] this occurs at 1300° C.

White and Taylor give 1200° C. as the temperature, and P. T. Walden [4] gives 1350° C.

Ferric oxide cannot exist above this temperature, and is probably reduced to FeO which combines with silica to form ferrous silicate.

Kinnison [5] in studying the reduction temperature of ferric oxide made up four mixtures as follows: (*a*) North Carolina kaolin, (*b*) same with silica added giving $Al_2O_3 : SiO_2 = 1 : 5.5$; (*c*) the same with $Al_2O_3 : SiO_2 = 1 : 9$; (*d*) a porcelain mixture. To each there was added $Fe_2(OH)_6$ to give 5 per cent Fe_2O_3. A black color developed suddenly in firing at the following temperatures: (*a*) 1390° C.; (*b*) 1360–70° C.; (*c*) 1310–20° C.; (*d*) 1210–20° C. The last gave a greenish-brown glass at 1240° C. His conclusions were: (1) that the smaller the $Al_2O_3 : SiO_2$ ratio, the lower the temperature of formation of the ferrous silicate; (2) that at comparatively low temperatures fluxes augment the coloring power of iron, and that at high temperatures the larger amount of fused material the more the iron is taken into solution and decreases the color. (3) In mixtures with large amounts of fluxes, the reduction is associated with solution, and the dissociation temperature is about 1210–20° C.

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[1] Orton and Staley, Third Report of Committee on Technical Investigation, Indianapolis, 1908.

[2] Clay Worker, July, 1904.

[3] High Temperature Measurements, p. 246.

[4] Jour. Amer. Chem. Soc., XXX, p. 1350.

[5] Trans. Amer. Ceram. Soc., XVI, p. 136, 1914.

Fluxing action of iron oxide.—Iron oxide is a fluxing impurity, lowering the fusing-point of a clay, and this effect will be more pronounced if the iron is in a ferrous condition or if silica is present.

While some regard finely divided iron oxide as one of the strongest fluxes,[1] others suggest that its maximum effectiveness is in clays [2] having the formula $Al_2O_3 \cdot 2.5\ SiO_2$, but is less active in those approaching the kaolinite formula. He states that the addition of 0.2 equivalents of Fe_2O_3 lowered the softening-point of clay $Al_2O_3–2.5\ SiO_2$ from cones 34 to 27.

Wheeler, in his work on the Missouri clays, formed the opinion that ferrous iron produces fluxing action about 150°–200° F. lower than ferric iron, whereas Orton and Staley, in their work referred to above, failed to find that any such great difference existed, although some was noticeable.[3]

Purdy and DeWolf, on the other hand, mention the case of a clay which fused to a globule at cone 16 under reducing conditions, but in an oxidizing fire did not fuse to a bead until cone 26.[4]

Hoffman [5] gives the softening temperatures for various ferrous silicates as follows:

$4FeO - SiO_2$	1280° C.	$2FeO - SiO_2$	1270° C.
$3FeO - SiO_2$	1220° C.	$3FeO - 2SiO_2$	1140° C.
$4FeO - 3SiO_2$	1120° C.		

Rieke, in testing the fluxing action of FeO on a mixture Al_2O_3-$2SiO_2$, found that 2.0 molecular equivalents reduced the fusion-point from cone 35 to cone 33.

Kuechler [6] found that 10 per cent Fe_2O_3 lowered the fusion-point of Florida kaolin, and fire-clay 6 and 6½ cones, respectively.

In burning a clay at low temperatures the hydrous ferric oxide (limonite) loses its water of hydration. Heating the clay to vitrification in a reducing atmosphere is believed to produce a ferrous silicate, which is seen on the brown, black, or greenish glassy portion of the surface of paving-brick and unglazed sewer-pipe.[7] When well-vitrified bricks show a red color it is thought by some that the iron oxide is merely dissolved in the vitrified mass and has not entered into combination.

[1] Bleininger and Brown, U. S. Bur. Stand., Tech. Pap., No. 7, p. 28, 1911.

[2] Cramer, Tonindus Zeit., Nos. 40–41, 1895.

[3] They quote Wheeler figures as 200° C., instead of 200° F., which is about 111° C.

[4] Ill. Geol. Surv., Bull. 4, p. 158, 1907.

[5] Trans. Amer. Inst. Min. Engrs., p. 682, 1899.

[6] Jour. Amer. Ceram. Soc., IX, p. 108, 1926.

[7] Ia. Geol. Surv., XIV, 59, 1904.

A low iron content is, therefore, desirable in refractory clays, and the average of a number of analyses of these shows it to be 1.3 per cent. Brick-clays, which are usually easily fusible, contain from 3 to 7 per cent of iron oxide.[1]

Effect of iron oxide on absorptive power and shrinkage of clay.—So far as the writer is aware no experiments have been made to discover the increased absorptive power of a clay containing limonite, although the clay soils show that the quantity of water absorbed is greater with limonite present. Senfft believes that it influences the power of clay for absorbing both gases and solutions.[2] This greater absorptive power may be accompanied by an increased shrinkage. The fire-shrinkage might also be great, because of the increased loss of combined water due to the presence of limonite.[3]

MANGANESE OXIDE

Although this compound is occasionally abundant in some residual deposits, where it may be worked as an ore, it is rarely present in large amounts in sedimentary clays.

Stout [4] notes that it is widely distributed in small quantities in the coal formation clays of Ohio. In eighty-three samples the average MnO content was .03 per cent, and the range from a trace to .27. The oxide acts as a flux, and according to Stout forms with silica the mineral rhodonite, $MnSiO_3$, which melts to a black viscous mass at about 1250° C.

Manganese oxide is sometimes used as a coloring-agent in building brick and floor tile, for producing gray and dark mottled shades. It is added to the clay in a powdered or granular form. It is said to give the best results in clays which are somewhat siliceous, low in iron oxide, and which reach their best state of structure at the temperature at which the manganese silicate is formed.

LIME

Lime is found in many clays, and in the low-grade ones may be present in large quantities. Quite a large number of minerals may serve as sources of lime in clays, but all fall into one of the three following groups:

1. Carbonates: Calcite, dolomite.

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[1] Many fire-brick of good refractoriness show as much as 2 or 3 per cent Fe_2O_2.

[2] Thonsubstanzen, Berlin, 1879, p. 21.

[3] See tests under Fire-shrinkage, Chap. V.

[4] Ohio Geol. Surv., 4th Ser., Bull. 26, p. 507, 1923.

2. Silicates containing lime, such as feldspar, and some garnets and amphiboles.

3. Sulphates: Gypsum.

The range of lime, as determined from a series of clay analyses, is as follows:[1]

AMOUNT OF LIME IN CLAYS

Kind of clay	I	II	III
Brick-clays.......	0.024	15.38	1.513
Pottery-clays.....	0.011	9.90	1.098
Fire-clays........	0.03	15.27	0.655
Kaolins..........	Tr.	2.58	0.47

I. Minimum.
II. Maximum.
III. Average.

Whenever the ultimate analysis of clay shows several per cent of lime (CaO) it is usually there as an ingredient of lime carbonate ($CaCO_3$), and in such cases its presence can be easily detected by putting a drop of muriatic acid or vinegar on the clay.[2] When present in this form it is apt to be finely divided, although it may occur as concretions or limestone pebbles, or as cylindrical bodies along rootlets.

The feldspars are the commonest source of lime among the silicates, oligoclase and anorthite being the usual lime-bearing varieties, but the amount of lime present as silicates is usually very low.

When lime is present as an ingredient of silicate minerals, such as those mentioned above, its presence cannot be detected with muriatic acid. Gypsum, which is found in a few clays, is often of secondary character, having been formed by the action of sulphuric acid on lime-bearing minerals in the clay. Since these three groups of minerals behave somewhat differently their effects will be discussed separately.

Effect of lime carbonate on clay.—Lime is probably most effective in the form of the carbonate, and if finely divided is an active flux. When clays containing it are burned, they not only lose their chemically combined water but also their carbon dioxide; but while the water of hydration passes off between 450° C. and 600° C., the carbon dioxide (CO_2) does not seem to go off until between 600° C.[3] and 725° C. In fact, it more probably passes off between 850° C.[1] and 900° C.[2] The result of driving off this gas, in addition to the chemically combined water, is to leave calcareous clays more porous than other clays up to the beginning of fusion.[3]

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[1] Bull. N. Y. State Museum, No. 35, p. 523. Owing to an error in the analysis of one of the brick clays, the averages in this table has been recalculated.

[2] See Minerals in Clay, Calcite.

[3] Montgomery and Groves (Trans. Amer. Ceram. Soc., XVIII, p. 214, 1916) found that in a small sample all the CO_2 was lost by 15 hours heating at 647° C.

If the burning is carried only far enough to drive off the carbonic-acid gas, the result will be that the quicklime thus formed will absorb moisture from the air and slake.[4] No injury may result from this if the lime is in a finely divided condition and uniformly distributed through the brick, but if, on the contrary, it is present in the form of lumps, the slaking and accompanying swelling of these may split the brick (Fig. 37).

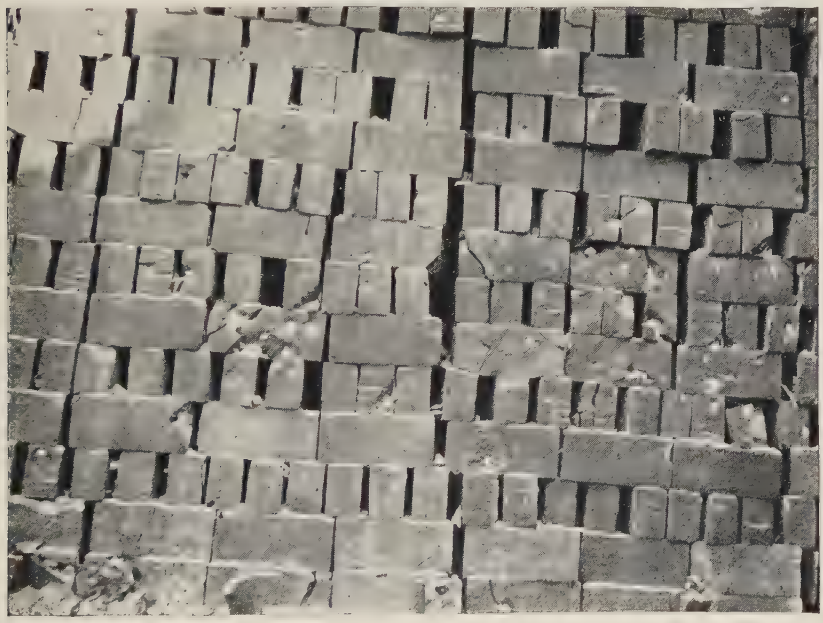

Fig. 37.—Bricks which have been cracked by lumps of limestone which were converted to lime, and air slaked.

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[1] Bourry, Treatise on Ceramic Industries, p. 103; also Kennedy, Trans. Amer. Ceram. Soc., IV, p. 146.

[2] See also Bleininger and Emley, Trans. Amer. Ceram. Soc., XIII, p. 618, 1911.

[3] Some bricks made from calcareous clays and burned at cones 1 to 3 show over 30 per cent absorption.

[4] According to Montgomery and Groves (Trans. Amer. Ceram. Soc., XVIII, p. 214, 1916), calcium hydroxide shows a distinct loss of weight between 430° C. and 439°, but this may vary with partial pressure of the gaseous water in the atmosphere.

Binns and Coats,[1] concluded that lime particles over 12-mesh in size are objectionable even in small amounts. From their experiments they thought that those passing 20-mesh were admissible up to 3 per cent, and those passing 36-mesh might be as high as 12 per cent.

A harder-burned product will resist the swelling action of the lime better than a softer-burned one.

It has also been suggested that dead burning the lime lumps, renders the material practically inactive with moisture, and so avoids injury due to slaking.[2]

If, however, the temperature is raised higher than is required simply to drive off the carbon dioxide, and if some of the mineral particles soften, a chemical reaction begins between the lime, iron, and some of the silica and alumina of the clay, the result being the formation within the clay of a new silicate of very complex composition. The effects of this combination are several: Lime in small quantities is thought to prevent the development of a good red color in firing. If, however, the lime is three times that of the iron then, as pointed out by Seger, the clay fires to a buff color. It should be remembered, however, that all buff-burning clays are not calcareous, and that a clay containing a low percentage of iron oxide may also give a buff body. Another effect of lime, if present in sufficient quantity, is to cause the clay to soften rapidly, thereby sometimes drawing the points of incipient fusion and viscosity within 41.6° C. of each other. This rapid softening of calcareous clays is one of the main objections to their use, and on this account also it is not usually safe to attempt the manufacture of vitrified products from them, but, as mentioned under Magnesia, the presence of several per cent of the latter substance will counteract this. It has also been found possible to increase the interval between the points of incipient fusion and viscosity by the addition of quartz and feldspar.[3]

One of the most extensive series of tests, are those made by R. Rieke,[4] who sought to determine in detail the effect of lime carbonate on kaolin. In his tests he mixed up different quantities of finely ground marble with Zettlitz kaolin, determining their shrinkage and porosity at different cones as indicated on p. 129.

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[1] Trans. Amer. Ceram. Soc., XIV, p. 218, 1912.

[2] Zimmerman, Tonindus. Zeit., XLIV, p. 993, 1920.

[3] The Collected Writings of H. Seger, Vol. I, p. 336.

[4] Ueber die Einwirkung von Marmor auf Zettlitzer kaolin, Sprechsaal, XXXIX, No. 38, 1906.

Shrinkage of Mixtures of Zettlitz Kaolin and Lime Carbonate

Per cent marble	1	3	5	10	20	30	40	50	60	70	80
Cone 05......	2.1	2	2.1	3.1	3.3	3.2	2.9	2.6	2.6	1.7	1.2
Cone 2......	3.5	4.1	4.2	4.4	3.4	3.1	2.6	2.4	3.0	1.7	1.0
Cone 5......	8.8	8.0	7.8	5.6	3.2	3.0	3.9	4.7	2.8	1.5	3.7
Cone 8......	9.8	9.2	8.8	7.1	3.0	4.3	9.6	15.0	4.2	4.6	5.9
Cone 10......	10.3	9.8	9.8	8.3	3.2	6.4	*	*	5.7	22.8	8.2
Cone 12......	11.9	11.2	11.1	9.4	3.8	6.6	*	*	6.0	*	9.5
Cone 14......	12.7	12.5	11.0	10.8	7.4	10.0	*	*	17.0	*	10.2

* Test-piece began to fuse and could not be measured.

Per Cent Porosity of Mixtures of Zettlitz Kaolin and Lime Carbonate

Per cent marble	1	3	5	10	20	30	40	50	60	70
Cone 05...	29.3	28.4	27.0	24.5	22.2	24.0	26.3	28.3	29.4	30.3
Cone 2...	25.7	23.4	21.3	19.8	21.1	22.8	25.3	27.3	30.8	42.5
Cone 5...	12.0	12.2	12.7	15.3	23.1	29.5	27.7	26.8	32.0	45.9
Cone 8...	8.7	9.7	9.9	11.9	24.6	29.2	14.4	......	33.2	42.0
Cone 10...	6.5	5.6	4.4	8.5	21.6	23.0	......	......	23.8	10.2
Cone 12...	4.4	2.4	1.5	3.4	21.0	17.7	......	......	22.6	
Cone 14...	2.0	0.3	0.3	0.2	9.1	7.7	......	......	4.1	

In order to determine the fusibility of the mixtures which did not fuse, the following special tests were made:

Per cent marble	0	1	3	5	10	20	30	40	50	60	70	80
Cone of fusion..	35*	35	31*	33	30†	15	15†	8*	7–8	16	12	23–24

*Above. †Nearly.

Rieke concludes from his experiments that:

1. Marble acts the reverse of magnesite in decreasing the shrinkage. That while a mixture of kaolin with 20 per cent magnesite shows the maximum shrinkage, a similar mixture of kaolin and marble shows a very low and almost uniform shrinkage throughout a great range of temperature.

2. The porosity of the burnt samples increases with an increase in the percentage of carbonate of lime, excepting at the lowest temperatures at which the carbon dioxide had not been entirely expelled. Only the mixtures carrying from 1 to 10 per cent of lime carbonate burn to a dense body at a temperature much below their fusing-point. A higher percentage of lime causes the points of vitrification and viscosity to draw close together.

3. The most easily fusible mixture is one having the formula $Al_2O_3 \cdot 2SiO_2 \cdot 2CaO$,[1] which fuses at cone 7–8.

Mixtures of the formula $Al_2O_3 \cdot 2SiO_2 \cdot 4CaO$; or $Al_2O_3 \cdot 2SiO_2 \cdot CaO$; and $2Al_2O_3 \cdot 2SiO_2$. CaO melt at about cone 16. If we have more than two molecules $Al_2O_3 \cdot SiO_2$, to one of CaO, very refractory mixtures result. With $6CaO \cdot Al_2O_3 \cdot 2SiO_2$, an easily fusible mixture is obtained, but an increase in the lime content raises it again.

The same writer has carried his experiments further, in determining the fusibility of lime-alumina-silica mixtures.[2] He points out that lime differs from magnesia in its fluxing action, in that its fusion curve shows not one, but three minima and two maxima, the last two corresponding to the formula $CaO \cdot Al_2O_3 \cdot 2SiO_2$ and $4CaO \cdot Al_2O_3 \cdot 2SiO_2$.

In the series of lime silica mixtures (Fig. 41), the fusion curve showed one maximum point corresponding to CaO, SiO_2, but that found by Day and Shepherd of $2CaO \cdot SiO_2$ was not observed. Two minima were found, one at about 1410° or between $CaO \cdot 0.7\ SiO_2$ and $CaO \cdot 0.8\ SiO_2$, and the other at 1420° C. Both of these agree with Day and Shepherd's observations, but their third minimum point was not found. In the lime-alumina-silica mixtures the ratios of alumina and silica employed were $Al_2O_3 \cdot SiO_2$; $Al_2O_3 \cdot 2SiO_2$; $Al_2O_3 \cdot 3SiO_2$; and $Al_2O_3 \cdot 4SiO_2$. To each of these the lime was added in increasing amounts.

The results of his tests are more clearly brought out by his diagrams, which are reproduced in Figs. 38–42.

N. B. Davis[3] found that the addition of lime to clay prevented cracking in drying, due probably to its flocculating action. The trouble was overcome by using 3, 4, 6 and 12 per cent, respectively. The lime is thought to form calcium salts with the acid silicates and silicic acid.

Many erroneous statements are found in books regarding the allowable limit of lime in clays, some writers putting it as low as 3 per cent; still a good building-brick can be made from a clay containing as much

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[1] This contained 46.3% CaO.

[2] R. Rieke, Ueber die Schmelzbarkeit von Kalk-Tonerde-Kieselsäuremischungen, Sprechsaal, XL, No. 44, p. 594, 1907.

[3] Trans. Amer. Ceram. Soc., XVII, p. 497, 1915.

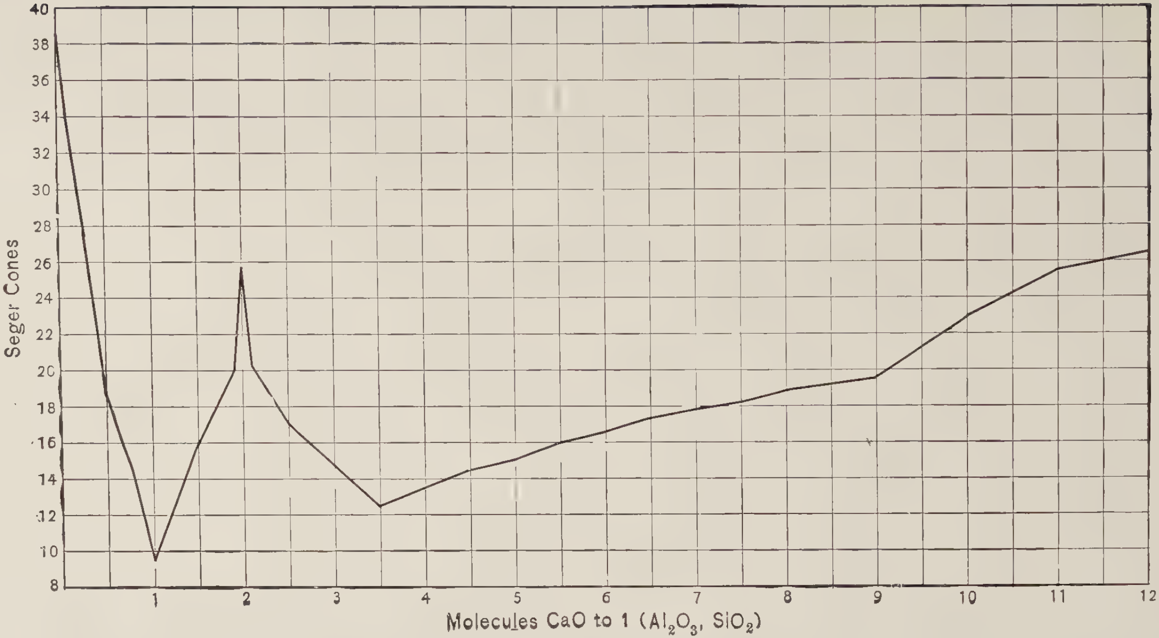

FIG. 38.—Diagram showing fusion-points of lime-alumina-silica mixtures. (After Rieke, Sprechsaal, XL, p. 625.)

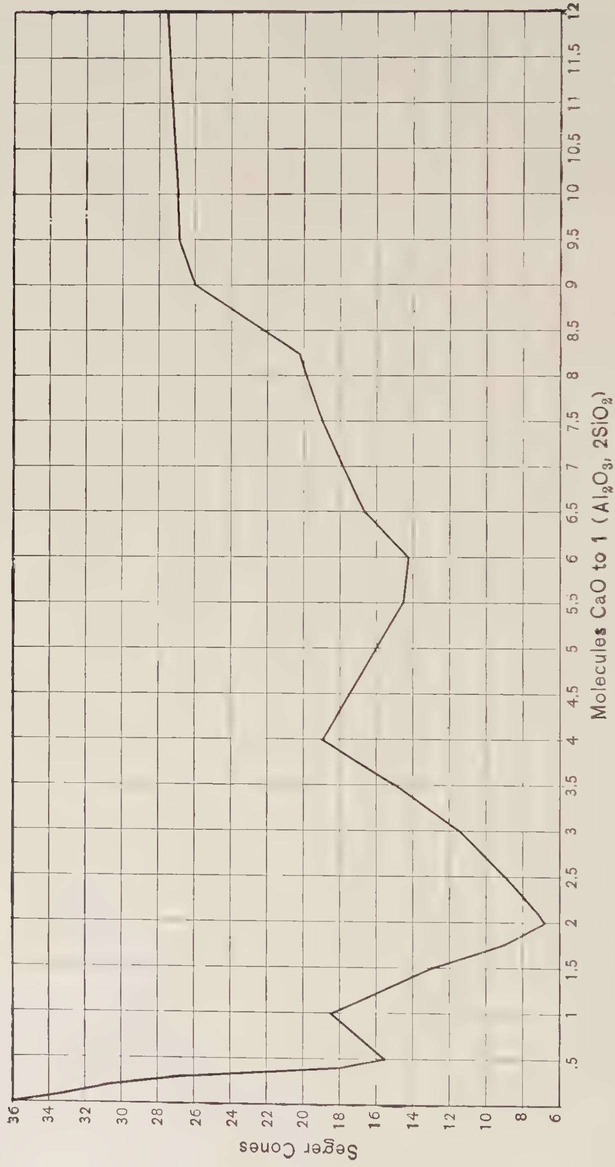

Fig. 39.—Diagram showing fusion-point of mixtures of CaO .1($Al_2O_3 \cdot 2SiO_2$). (After Rieke, Sprechsaal, XL, p. 612.)

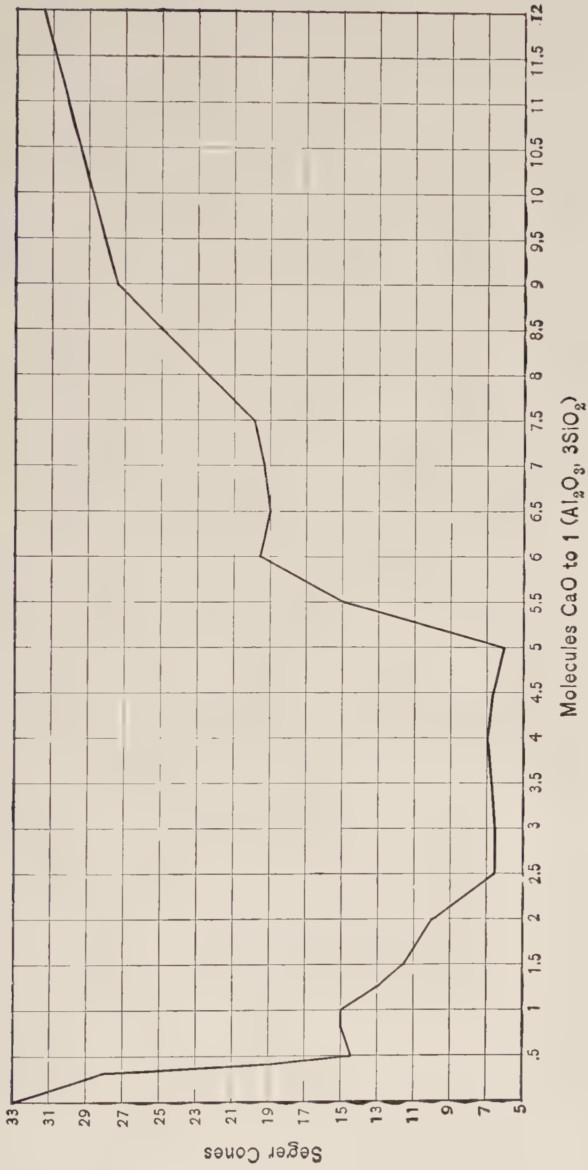

Fig. 40.—Diagram showing fusing-points of mixtures of CaO and $1(Al_2O \cdot 3SiO_2)$. (After Rieke, Sprechsaal, XL, p. 610.)

as 20 or 25 per cent of lime carbonate, provided it is in a finely divided condition,[1] and a vitrified ware is not attempted. If, however, that

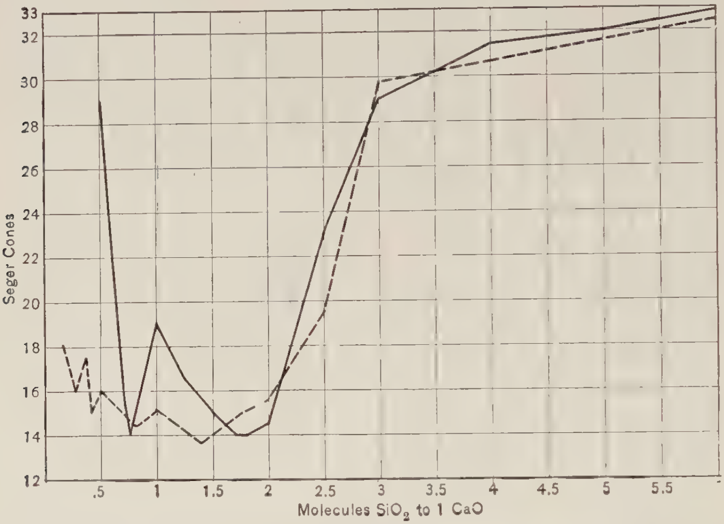

FIG. 41.—Diagram showing fusion-points of lime-silica mixtures. (After Rieke, Sprechsaal, XL, p. 595.) Dotted lines represents curve obtained by Boudouard.

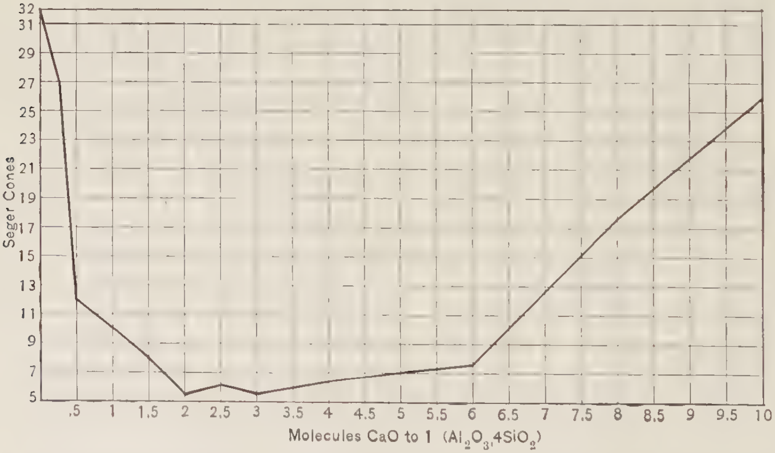

FIG. 42.—Diagram showing fusion-points of mixtures of CaO and ($Al_2O_3 \cdot 4SiO_2$). (After Rieke, Sprechsaal, XL, p. 626.)

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[1] For analyses and uses of calcareous clays, see H. Ries, Clays and Shales of Michigan, Mich. Geol. Surv., VIII, Pt. I; and E. R. Buckley, Clays and Clay Industries of Wis., Wisconsin Geol. Surv., Bull. 2, Economic Series.

quantity of lime is contained in the clay in the form of pebbles, then much damage may result from bursting of the bricks, when the lumps of burned lime slake by absorbing moisture from the air.

Clays containing a high percentage of lime carbonate are used in the United States, especially in Michigan, Wisconsin, and Illinois, for making common bricks, common earthenware, roofing-tile, and some terra-cotta, and the highly calcareous character of some brick-clays is shown by the following analyses. Of these No. II is the most calcareous that the writer has ever examined.

Analyses of Calcareous Clays

	I	II
Silica (SiO_2)	44.15	18.62
Alumina (Al_2O_3)	10.00	3.23
Ferric oxide (Fe_2O_3)	4.08	1.26
Lime (CaO)	13.30	41.30
Magnesia (MgO)	1.50	.42
Potash (K_2O)	1.55	None
Soda (Na_2O)	By diff.	2.42
Water (H_2O)	12.13	
Carbon dioxide (CO_2)	11.34	32.50
Organic matter	1.95	
Total	100.00	99.75
Total fluxes	20.43	42.98

I. Ionia, Mich. A. N. Clark, analyst. Mich. Geol. Surv., VIII, Pt. I, p. 53.
II. Seguin, Tex. O. H. Palm, analyst.

Effect of lime-bearing silicates.—The effect of these is much less pronounced than that of lime carbonate. They contain no volatile elements, and hence do not affect the shrinkage to the extent that lime carbonate does. They serve as fluxes,[1] but do not cause a rapid softening of the clay.

Effect of gypsum.—Gypsum in clay has probably often been formed by sulphuric acid, liberated by the decomposition of iron pyrite, acting on lime carbonate. Lime, if present in the form of gypsum, seems to behave differently from lime in the form of carbonate, although few clays contain large percentages of it.

Gypsum, as already shown,[2] is a hydrous sulphate of lime. In calcining gypsum for making plaster of Paris, the chemically combined water is driven off at 250° F., but only a portion of the sulphuric acid is driven off at a low red heat, the balance passing off at a much higher temperature. To illustrate this a mixture[1] consisting of 75 per cent of a white-burning clay and 25 per cent of nearly pure white gypsum was made up. This mixture contained 15.11 per cent of combined water and 11.65 per cent of sulphur trioxide (SO_3), and was burned at a number of different temperatures with the following results:

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[1] See also under Alkalies.

[2] Chapter II, Minerals in Clay.

Table Showing Loss in Weight Gypsum—Clay Mixture in Firing

Temperature	Loss in weight, per cent	
	Sample No. 1	Sample No. 2
860° C. (1580° F.).....	11.60	11.50
1000° C. (1832° F.).....	13.18	12.59
1100° C. (2012° F.).....	19.93	19.58
1200° C. (2192° F.).....	23.15	23.05
1300° C. (2372° F.).....	23.21	23.11

These figures show that at 860° C. the loss had not exceeded the amount of combined water contained in the mass; at 1000° C. the loss was not equal to the sum of the water contained in the clay and gypsum; a large loss occurred between 1100° and 1200° C., while between the latter temperature and 1300° C. the loss was exceedingly small. Therefore, even at 1300° C., or slightly above the theoretic melting-point of cone 8, there was still over 3 per cent of what would be considered volatile material remaining in the mixture. It is presumed that this represents sulphur trioxide which has not been driven off.

The presence of silica is said to facilitate the decomposition of the calcium sulphate, and the evolution of the SO_3 is thought to cause some of the swelling or blistering seen in some wares after burning.

MAGNESIA

Magnesia (MgO) rarely occurs in clay in larger quantities than 1 per cent. When present, its source may be any one of several classes of compounds, that is silicates, carbonates, and sulphates.

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[1] N. J. Geol. Surv., VI, p. 63, 1904.

The range of magnesia in several classes of clays, as figured from a number of analyses is as follows:[1]

AMOUNT OF MAGNESIA IN CLAYS

Quality	I	II	III
Brick-clays	0.02	7.29	1.052
Pottery-clays	0.05	4.80	0.85
Fire-clays	0.02	6.25	0.513
Kaolins	Tr.	2.42	0.223

I. Minimum.
II. Maximum.
III. Average.

In the majority of clays the silicates, no doubt, form the most important source, and minerals of this type carrying magnesia are the black mica or biotite, hornblende, chlorite, and pyroxene. These are scaly or bladed minerals, of more or less complex composition, and containing from 15 per cent to 25 per cent of magnesia. The biotite mica decomposes readily, and, its chemical combination being thus destroyed, the magnesia is set free, probably in the form of a soluble compound, which may be retained in the pores of the clay. Hornblende is probably not an uncommon constitutent of some clays, especially in those which are highly stained by iron, and have been derived from dark-colored igneous rocks. Like biotite, it alters rather rapidly on exposure to the weather. Dolomite, the double carbonate of lime and magnesia, is no doubt present in some clays, and would then serve as a source of magnesia. Magnesium sulphate, or Epsom salts, probably occurs sparingly in clays, and might form a white coating either on the surface of clay spread out to weather, or else on the ware in drying. It is most likely to occur in those clays which contain pyrite, the sulphide of iron (FeS_2), for the decomposition of the latter would yield sulphuric acid, which, by attacking any magnesium carbonate in the clay, might form magnesium sulphate. This substance has a characteristic bitter taste. On heating, both magnesium carbonate and dolomite have been supposed to lose their CO_2 between 400° C. and 600° C.[2]

Magnesia was for many years regarded as similar to lime in its fluxing action. The experiments of Mäckler[1] have indicated, however, that its effect was quite different.

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[1] Bull. N. Y. State Museum, No. 35, p. 523. Owing to an error in the analysis of one of the brick clays, the averages in this table has been recalculated.

[2] Brill's work (Zeitchr. Anorg. Chem., XLV, p. 277, 1905) shows that MgCO, begins to lose some CO_2 at 255° C., and additional quantities at 295°, 325°, 340°, 380°, 405°, and 510° C. These points are believed to show the successive formations and breaking up of various basic carbonates.

In order to prove this point he selected a clay which was free from lime or magnesia, and in its raw and burned condition had the composition shown in following table:

ANALYSIS OF CLAY USED BY MÄCKLER

	I	II
Loss on ignition	7.07	
Silica (SiO_2)	63.25	68.06
Alumina (Al_2O_3)	22.97	24.72
Ferric oxide (Fe_2O_3)	4.98	5.36
Lime (CaO)		
Magnesia (MgO)		
Alkalies (Na_2O, K_2O)	2.07	2.22
	100.34	100.36

I. Raw.
II. Burned.

To one hundred parts by weight of this clay, either lime or magnesium carbonate was added in the proportions given in the table below, the percentages given in parenthesis representing the quantity of lime or magnesia contained in the amount of carbonate added. The physical tests of these mixtures are also given.

It will be seen here that the effect of magnesia was quite different from that exerted by the lime. The mixtures containing magnesia did not vitrify suddenly, as did the limy clays; nor did the magnesia exert as strong a bleaching action on the iron, and the points of incipient fusion and viscosity were also separated.

PHYSICAL TESTS ON MÄCKLER'S MIXTURES

	Water required	Air-shrinkage	Loss of weight in firing	Fire-shrinkage cone numbers				
				010	05	1	3	5
A. Clay alone	28.8	6.4	9.8	0.1%	3.5	7.2	7.9	6.7
B. Clay + 25$CaCO_3$(14CaO)	31.1	8.4	14.3	1.4	1.8	*		
C. Clay + 12.5$CaCO_3$(7CaO)	33.6	8.3	10.4	1.0	1.7	†		
D. Clay + 21$MgCO_3$(10MgO)	34.0	8.2	16.3	0.6	3.0	11.7	11.9	*
E. Clay + 10.5$MgCO_3$(5MgO)	32.4	7.5	11.1	1.7	3.7	11.1	11.3	†

*Melted †Warped

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[1] Tonindustrie-Zeitung, Vol. XXVI, p. 705, 1902.

With a mixture of kaolin and magnesia similar results were obtained. The mixture of kaolin and magnesia showed a higher shrinkage at the beginning of the burning than the kaolin alone, and then increased but little until a high temperature was reached, when the shrinkage suddenly began again. A hard body was obtained at cone 1 with the kaolin-magnesia mixture.

The effect of magnesia therefore, if present in sufficient quantity, is to act as a flux and make the clay soften slowly, instead of suddenly as in the case of calcareous clays. The results mentioned above have been corroborated in this country by Hottinger.[1] An important characteristic of magnesian clays is, that they can be made into wares of extreme length and very thin walls, which may be nearly vitrified without warping.[1]

Barringer [2] has pointed out that the action of magnesia depends largely on the composition of the clay; in bodies containing a number of active fluxes, and which vitrify at a low temperature, it has a marked influence on the fusing point and temperature of the vitrifying stage, but, " as the number and character of the bases change in going towards high-fire products, the influence of magnesia lessens considerably."

To the data supplied us by Mäckler and Barringer, there must be added a more extensive series, embodying the results of R. Rieke's [3] work on kaolin-magnesite mixtures, of which he determined the linear shrinkage, porosity and fusibility. The results of the first two series

Per Cent Linear Shrinkage of Zettlitz Kaolin and Magnesite

Per cent magnesite	0	1	3	5	10	20	30	40	50	60	70	80	90
Cone 09........	2.0	2.2	2.4	2.5	2.7	2.8	3.1	3.1	3.7	3.8	3.3	3.0	2.7
Cone 05........	2.7	3.0	2.8	3.1	3.2	3.6	3.4	4.1	5.4	5.5	5.1	5.5	5.7
Cone 1........	2.8	3.1	3.1	3.1	3.1	3.0	3.8	4.8	5.7	5.5	5.0	5.6	6.2
Cone 3........	6.8	7.5	8.2	8.8	10.6	12.2	11.2	9.2	7.5	5.6	5.0	5.9	7.3
Cone 5........	8.4	9.1	10.7	11.3	12.3	12.5	11.7	9.3	8.5	7.8	7.0	7.9	10.4
Cone 7........	10.5	10.5	11.2	12.6	13.5	13.4	13.0	9.8	9.5	8.0	7.6	8.9	11.0
Cone 10........	12.5	12.6	13.4	13.6	13.4	13.5	11.9	....	24.0	18.9	7.7	10.5	23.0
Cone 12........	12.8	12.6	13.4	13.1	13.4	13.6	9.2 bls'd	....	....	23.0	10.0	16.2	25.3
Cone 15........	12.5	12.3	12.5	12.8	14.1	12.5 bls'd	....	....	....	25.3	13.8	21.1	28.2

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[1] Hottinger, Trans. Amer. Ceram. Soc., V, p. 130, 1903.

[2] Trans. Amer. Cer. Soc., VI, p. 86, 1904; see also Rev. Mat. Constr. Trav. Pub., CXL, p. 67, 1921.

[3] Sprechsaal, Nos. 46–48, 1905.

PERCENTAGE POROSITY OF ZETTLITZ KAOLIN AND MAGNESITE

Per cent magnesite	0	1	3	5	10	20	30	40	50	60	70	80	90
Cone 09	30.1	29.9	30.8	30.5	31.6	34.6	41.7	42.4	49.5	53.6	Undetermined mostly over 50 per cent		
Cone 05	30.5	29.2	28.8	29.2	30.0	31.1	35.9	37.5	37.9	40.2			
Cone 1	30.6	28.2	29.6	29.2	30.8	31.6	36.2	37.7	38.0	41.7			
Cone 3	19.4	17.0	14.3	12.6	11.1	11.2	15.5	23.8	34.8	44.4			
Cone 5	16.1	12.7	8.0	6.4	4.2	2.8	11.7	21.8	25.5	43.3			
Cone 7	9.7	10.0	6.3	0.4	0.3	0.1	8.3	17.6	18.0	18.7			
Cone 10	2.1	1.8	0.4	0.1	0.1	0.1	3.1	....	0.5	8.5	43.2	39.6	11.7
Cone 12	2.4	2.0	0.5	0.0	0.0	0.0	...	....	....	2.0	38.0	30.2	8.2
Cone 15	1.1	0.7	0.2	0.0	0.0	....	....	....	....	0.0	28.1	17.3	3.4

of tests are given in the accompanying tables, while the fusion points are given in Fig. 43. It will be noticed there that the fusion point gradually falls until a content of 45 per cent magnesite is reached, after which it again rises.

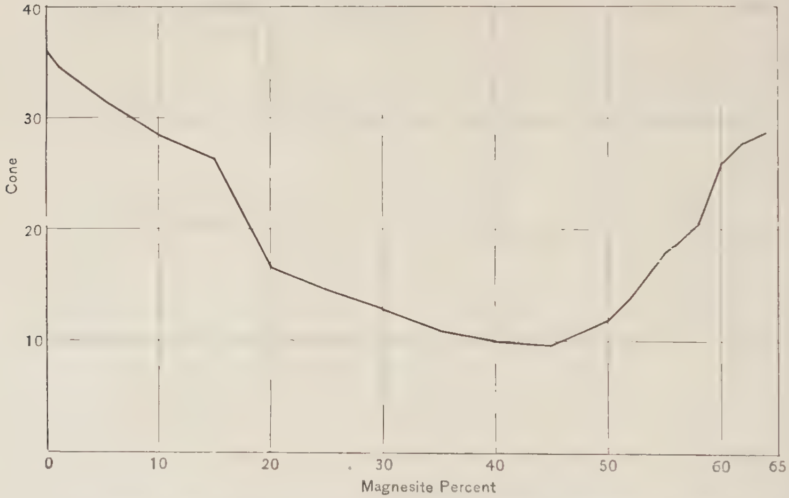

FIG. 43.—Diagram showing fusibility of kaolin-magnesite mixtures. (After Rieke, Sprechsaal, Nos. 46–48, 1905.)

Of equal interest are a later series of experiments, in which quartz was added to the original mixture, the results being shown in tabulated form on the following pages.

ALKALIES

The alkalies commonly present in clays include potash (K_2O), soda (Na_2O), and ammonia (NH_3). There are other alkalies, but they are probably of rare occurrence.

Ammonia is no doubt present in some raw clays, judging from their odor, and it may possibly exert some effect on the physical structure of the clay, it being found that the bunches of grains in a clay tend to separate more easily, when the clay is agitated with water, if a few drops of ammonia are added. As ammonia is easily volatile, it leaves the clay as soon as the latter is warmed, and therefore plays no part in the burning of the clay. The two other common alkaline substances, potash and soda, are more stable in their character, and are therefore sometimes termed *fixed alkalies*. These have to be reckoned with in burning, for they are present in nearly every clay.

The amount of total fixed alkalies contained in a clay varies from a mere trace in some to 9 per cent in others. The range of alkalies in several classes of clays was determined to be as follows:[1]

AMOUNT OF TOTAL ALKALIES IN CLAYS

	I	II	III
Kaolins..........	0.1	6.21	1.01
Fire-clays........	0.048	5.27	1.46
Pottery-clays.....	0.52	7.11	2.06
Brick-clays.......	0.17	15.32	2.768

I. Minimum.
II. Maximum.
III. Average.

Several common minerals may serve as sources of the alkalies. Feldspar may supply either potash or soda. Muscovite, the white mica, contains potash. Greensand, or glauconite, contains potash. Other minerals, such as hornblende or garnet, might serve as sources of the alkalies, but are unimportant, as they are rarely present in clays in large quantities.

Orthoclase, potash feldspar, contains 17 per cent of potash (K_2O), while the lime-soda feldspars contain from 4 to 12 per cent of soda (Na_2O), according to the species. The lime-soda feldspars fuse at a lower temperature than the potash ones, but are also less common.[2]

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[1] Bull. 35, N. Y. State Museum, p. 515.

[2] Seger, Ges. Schrift, p. 413.

RIEKE'S TESTS ON KAOLIN, QUARTZ-MAGNESITE MIXTURES

No. of mixture.	Per cent of			Cone 09.		Cone 2.		Cone 5.		Cone 6–7.		Cone 8–9.		Cone 11.		Cone 13–14.		Cone 15.		Cone of fusion.
	Kaolin.	Qtz.	Mag.	S.[1]	P.[2]	S.	P.	S.	P.	S.	P.	S.	P.	S.	P.	S.	P.	S.	P.	
1	90	10	..	2.0	28.9	4.4	23.0	7.3	16.0	8.8	13.2	9.2	11.0	10.4	7.1	11.5	3.7	12.7	0.5	+34
2	90	5	5	2.2	30.6	6.3	21.0	10.3	9.6	10.7	5.5	11.8	0.9	12.8	0	12.4	0	13.2	0	30
3	80	20	....	1.8	28.9	4.2	23.9	6.5	19.1	7.6	16.3	8.5	14.7	9.7	9.4	12.6	5.3	13.1	0.9	33
4	80	15	5	2.1	30.1	5.3	22.2	9.0	15.4	10.6	9.8	12.5	2.0	13.6	0	13.2	0	13.5	0	−29
5	80	10	10	2.1	31.8	7.1	19.0	10.1	11.1	11.9	3.4	12.7	0	12.3	0	12.2	0	12.5	0	20
6	80	5	15	2.4	33.3	9.1	14.3	11.0	10.4	12.9	0.3	12.5	0	12.6	0	12.8	0	12.8	0	−19
7	70	30	....	1.5	29.5	3.9	24.3	5.2	20.9	6.2	19.0	7.3	16.8	9.2	11.4	10.7	7.2	12.0	3.4	31–32
8	70	25	5	1.4	29.8	5.4	22.8	7.5	17.0	8.9	11.0	12.4	3.0	12.8	0.3	13.9	0	13.9	0	27–28
9	70	20	10	1.7	31.5	5.7	20.2	9.3	15.5	11.9	4.8	12.4	0.0	12.5	0	12.5	0	12.7	0	+19
10	70	15	15	2.1	33.4	7.2	20.9	9.6	15.3	11.6	4.5	11.7	0.1	11.7	0	11.9	0	11.7	0	15–16
11	70	10	20	2.0	34.3	7.3	21.8	10.5	13.5	11.3	4.2	11.4	0.1	11.3	0	11.3	0	.....	.....	14–15
12	70	5	25	2.2	34.5	8.5	19.5	10.6	14.3	11.0	1.8	11.1	0.2	10.5	0	10.6	0	.....	.....	14
13	60	40	....	1.4	27.4	3.2	23.9	4.0	23.2	5.4	20.3	5.4	19.9	8.1	13.8	9.8	10.9	12.4	4.4	31
14	60	35	5	1.4	30.0	4.7	24.4	5.2	22.4	8.2	16.8	9.7	14.7	12.0	4.2	13.0	0.2	13.2	0	20–26
15	60	30	10	1.7	30.5	5.4	23.7	6.1	22.4	9.4	13.9	11.0	5.5	12.6	0.8	12.7	0	13.3	0	−19
16	60	25	15	1.9	33.7	5.6	24.0	6.3	23.1	9.2	12.7	10.5	9.6	12.8	0.7	13.0	0	.....	.....	−15
17	60	20	20	2.0	34.0	6.4	24.3	7.0	24.0	9.3	10.7	10.3	10.8	12.3	0.6	15.0	0	.....	.....	−14
18	60	15	25	2.3	34.6	6.7	25.3	7.2	24.1	9.8	14.8	10.1	11.8	10.9	4.9	11.0	1.1[3]	.....	.....	−(13–14)
19	60	10	30	2.5	36.7	6.8	26.7	7.5	25.5	10.7	13.5	11.1	12.2	13.0	7.8	.....	.....	.....	.....	+12
20	60	5	35	2.6	38.4	6.7	28.7	7.1	28.2	11.7	13.4	12.6	8.0	.....	0	.....	.....	.....	.....	+11
21	50	50	....	0.8	27.3	2.3	24.8	2.7	25.0	3.8	23.0	4.5	21.0	6.5	16.8	8.2	13.9	11.3	10.4	29–30
22	50	45	5	1.0	28.9	3.6	24.5	4.8	22.4	6.5	17.8	7.9	12.6	9.4	5.8	10.2	4.8	12.3	.6	−20
23	50	40	10	1.3	29.7	4.1	24.6	5.4	22.9	7.9	17.0	8.5	12.6	9.0	6.6	10.6	0.8	11.9	0	+(15–16)
24	50	30	20	1.7	32.5	5.7	24.8	5.8	24.5	6.7	21.1	8.9	14.6	10.4	9.2	.....	.....	.....	.....	+13
25	50	20	30	2.2	35.8	5.2	30.0	5.7	28.9	7.2	21.4	10.8	14.7	11.6	12.9	.....	.....	.....	.....	11–12
26	50	10	40	3.0	40.1	7.1	31.2	7.2	31.0	7.5	29.2	10.0	19.4	.....	.....	.....	.....	.....	.....	11

[1] S. = linear shrinkage, per cent.

[2] P. = porosity, per cent.

[3] Blistered.

RIEKE'S TESTS ON KAOLIN, QUARTZ-MAGNESITE MIXTURES

No. of mixture.	Per cent of			Cone 09.		Cone 2.		Cone 5.		Cone 6–7.		Cone 8–9.		Cone 11.		Cone 13–14.		Cone 15.		Cone of fusion.
	Kaolin.	Qtz.	Mag.	S.[1]	P.[2]	S.	P.	S.	P.	S.	P.	S.	P.	S.	P.	S.	P.	S.	P.	
27	50	5	45	3.2	42.2	6.7	35.8	7.7	31.5	9.1	29.4	9.5	19.9	.....	.....	.....	.....	.....	.....	−11
28	40	60	....	0.4	28.4	2.0	25.3	1.9	25.5	2.8	24.3	3.9	22.1	4.7	18.8	6.2	15.7	7.8	12.8	−29
29	40	55	5	0.4	28.6	3.7	22.4	5.2	20.3	5.8	18.7	5.8	18.0	6.1	14.6	8.1	10.8	12.3	7.2	+17
30	40	50	10	1.0	30.1	5.0	22.0	6.0	20.0	6.8	17.5	6.1	17.2	7.3	11.0	8.4	5.2	.....	.....	+(13–14)
31	40	40	20	1.4	33.2	4.9	33.1	6.8	22.3	7.5	19.7	7.1	18.8	9.8	9.7	.....	.....	.....	.....	−12
32	40	30	30	1.9	35.3	6.1	29.5	6.7	25.3	10.3	15.5	9.7	16.5	.....	.....	.....	.....	.....	.....	10
33	40	20	40	2.7	39.8	5.9	32.9	7.6	28.4	10.1	22.9	8.3	24.1	.....	.....	.....	.....	.....	.....	−11
34	40	10	50	3.4	43.9	6.0	37.9	8.9	31.8	11.7	26.1	21.5	3.5	22.8	0.1	.....	.....	.....	.....	12
35	40	5	55	3.8	45.7	5.8	41.5	8.2	35.9	10.5	30.9	23.4	0.9	26.0	0	26.5	0	27.6	0	17
36	30	70	....	0.4	27.6	1.2	24.6	1.2	24.0	1.8	23.7	2.7	22.3	3.4	19.7	4.8	18.0	6.2	14.7	27–28
37	30	65	5	0.6	27.7	2.7	21.8	3.5	21.6	3.7	20.6	3.5	20.0	4.2	17.2	4.7	16.6	10.9	11.8	+16
38	30	60	10	0.6	29.1	3.0	23.6	4.8	20.7	5.3	20.7	3.4	20.3	5.0	16.3	5.1	17.9	12.7	0.4	−16
39	30	50	20	0.8	32.5	3.5	26.2	5.8	21.9	6.9	18.2	5.3	20.7	8.8	12.2	(11.5)	0	.....	.....	13–14
40	30	40	30	1.1	34.3	3.9	29.6	6.3	25.2	8.0	19.5	7.3	21.2	.....	.....	.....	.....	.....	.....	−10
41	30	30	40	1.9	38.4	4.7	33.2	6.7	29.1	10.7	21.2	9.7	19.1	.....	.....	.....	.....	.....	.....	−(10–11)
42	30	20	50	2.7	43.7	4.8	38.6	7.2	35.0	8.4	31.3	23.2	0.2	22.3	0	.....	.....	.....	.....	11
43	30	10	60	3.4	47.9	7.2	39.8	7.5	38.9	10.7	32.5	21.5	8.3	25.1	1.1	25.9	0	27.5	0	+19
44	30	5	65	3.7	49.8	6.5	46.0	7.6	41.7	7.7	40.0	8.8	37.9	9.0	33.5	12.0	29.8	24.7	14.3	−31

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[1] S. = linear shrinkage, per cent

[2] P. = porosity, per cent.

[3] Blistered.

Muscovite mica contains nearly 12 per cent of potash, and may contain a little soda. If present in quantity and of fine texture it may serve as a flux. (See under Mica.)

We therefore see that the minerals supplying alkalies are all silicates of complex composition. Each has its fixed melting-point, and the temperature at which the alkalies flux with the clay will depend on the containing mineral, and also on the size of the grains. If the alkali-bearing mineral grains decompose, the potash or soda are set free and form soluble compounds.[1]

Alkalies are considered to be the most powerful fluxing material that the clay contains, and, if present in the form of silicates, are a desirable constituent, except in clays of a refractory character. On account of their fluxing properties they serve, in burning, to bind the particles together in a dense, hard body, and permit a white ware, made of porous-burning clays, to be burned at a lower temperature. In the manufacture of porcelain, white earthenware, encaustic tiles, and other wares made from white-burning clays and possessing an impervious or nearly impervious body, feldspar is an important flux.

According to the experiments of Berdel [2] on kaolin, quartz, feldspar bodies, the action of feldspar on the vitrification of bodies is noticeable at cone 1, but its effect on high-heat bodies starts with the melting-point of feldspar at cone 9. The vitrifying action of feldspar becomes greater the finer the grain is, and to such an extent that very fine feldspar may vitrify Zettlitz kaolin at cone 2.

Alkalies alone seem to exert little or no coloring influence on the burned clay, although in some instances potash appears to deepen the color of a ferruginous clay in burning.

TITANIUM

Titanium is an element which is found in several minerals, some of which are more common in clays than is usually imagined, although they appear rare because they are seldom found in large quantities. The two commonest of these, rutile and ilmenite, have already been referred to. So far as known, neither of these is ever found in clays in sufficiently large grains to be visible to the naked eye, so that a microscopic examination would be necessary to identify them. Although titanium is such a common constituent of clay, it is rarely shown in an analysis, because its determination by chemical methods is attended with more or less difficulty and is rarely carried out. In the ordinary process of chemical analysis it is usually included with the alumina.

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[1] See Origin of Clay, Chapter I.

[2] Sprechsaal, Nos. 2–11, 1904.

As early as 1862 Riley [1] referred to the universal occurrence of titanic oxide in clay, and, in a series of English ones, found from .42 to 1.05 per cent. Since that time a number of additional occurrences have been noted, as follows:

Twenty-one New Jersey clays, 1.06 to 1.93 per cent; [2] a series of Pennsylvania clays, .85 to 4.30 per cent; [3] eleven Ohio coal-measure clays, 0.16 to 1.68 per cent; [4] fire-clays from St. Louis, 1 to 1.91 per cent; [5] thirty-five clays and sands from Virginia Coastal Plain, .0 to 1.88 per cent; [6] one hundred Texas clays, .0 to 2.12 per cent.[7]

Somers [8] has noted its occurrence in many high grade clays, when examined under the microscope.

Among the foreign observers, Vogt [9] has noted percentages as high as 2.08, and Kovar [10] the unusually high percentage of 10.06, while Odernheimer found up to 4.6 per cent in certain basaltic residual clays from the Duchy of Nassau. The fact that most of it was soluble in a 20 per cent hydrochloric-acid solution would suggest its being ilmenite.

Effect of titanium.—H. Seger and E. Cramer, of Berlin,[11] endeavored to determine the effect of titanium on clay by burning artificial mixtures of this material and kaolin. Two samples of Zettlitz kaolin (containing 98.5 per cent clay substance) were mixed with 6.5 per cent and 13.3 per cent titanium oxide respectively; both were then heated to a temperature above the fusing-point of iron, with the result that, while the first softened considerably on heating and showed a blue fracture, the second fused to a deep-blue enamel.

A second series of mixtures, consisting each of one hundred parts of kaolin, with 5 per cent and 10 per cent of silica respectively, showed no signs of fusion, and burned simply to a hard white body, thus indicating that the titanium acts as a flux at a lower temperature than quartz.

More recently the author [12] has shown that even small amounts of titanium lower the refractoriness of a clay. In these experiments a white-burning sedimentary clay fusing at cone 34 was mixed with amounts of ½, 1, 2, 3, 4, and 5 per cents of very finely ground rutile.

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[1] Quart. Jour. Chem. Soc., XV, 311, 1862.

[2] Cook and Smock, Report on the Clays of New Jersey, 1878, p. 276.

[3] Second Pa. Geol. Surv., MM, p. 261 et seq.

[4] Orton, Ohio Geol. Surv., VII, Pt. I

[5] Wheeler, Mo. Geol. Surv., XI, p. 56.

[6] Ries, Va. Geol. Surv., Bull. II.

[7] Bull. Univ. Tex., 102, 1908.

[8] U. S. Geol. Surv., Bull. 708.

[9] Tonindustrie-Zeitung, XXVII, 1247, 1903.

[10] Sprechsaal, 1891, p. 106.

[11] Seger's Collected Writings, I, p. 519.

[12] N. J. Geol. Surv., Fin. Rept., VI, p. 71, 1904.

These mixtures were then formed into small cones and tested in the Deville furnace, the results of these tests being shown graphically by the curve in Fig. 44. In this figure the vertical line at the left represents the cone number of the Seger series,[1] and the horizontal line at the bottom the per cent of titanium oxide. No. VII, at the extreme left, represents the fusion-point of the clay alone, while I, II, etc., indicate respectively the fusion-points of the clay and titanium mixtures. From this it will be seen that even one-half per cent of titanium oxide lowered the fusing-point of the clay half a cone, while 5 per cent lowered it two cones. All the mixtures, when heated to cone 27, were apparently vitrified, and showed a deep-blue fracture. This coloration was, however, destroyed by the presence of a few per cent of silica. At lower temperatures (cone 8) a mixture containing 5 per cent of titanium oxide burned yellow.

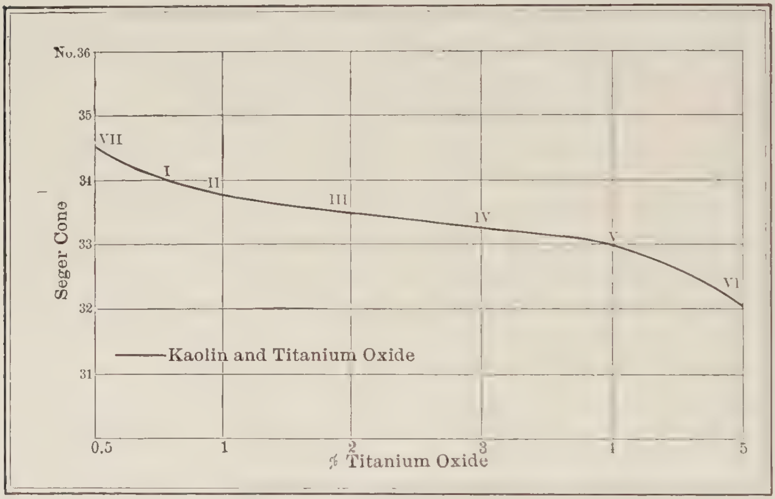

FIG. 44.—Curve showing effect of titanium oxide on white sedimentary kaolin. (After Ries, N. J. Geol. Surv., Fin. Rept., VI, p. 71, 1904.)

A recent series of experiments by Rieke [2] form an interesting continuation of those by the author (described above). He made up a series of mixtures of chemically pure TiO_2 and Zettlitz kaolin, determining their fusing-points with the following results:

---

[1] See Fusibility, Chapter V.

[2] Sprechsaal, XLI, p. 406, 1908.

Fusion Points of Kaolin-Titanium Oxide Mixtures

Kaolin, per cent	TiO_2, per cent	Cone of fusion	Kaolin, per cent	TiO_2, per cent	Cone of fusion
100	....	35	40	60	20
90	10	30	30	70	+20
80	20	−26	20	80	−26
70	30	20	10	90	26
60	40	−20	....	100	−27
50	50	19−20			

The heat was raised at the rate of one cone in 4–5 minutes. With very much slower heating the fusion-points lay slightly higher for mixtures with 40 per cent or more of TiO_2.

A similar series of mixtures in which the kaolin was replaced by alumina or silica showed that the titanium was less effective. The results of these other series were as below.

Fusion Points of Alumina-Titanium Oxide Mixtures

Alumina, per cent	TiO_2, per cent	Cone of fusion	Alumina, per cent	TiO_2, per cent	Cone of fusion
100	....	42	40	60	33−34
80	20	37	30	70	31
70	30	−35	20	80	−29
60	40	33	10	90	−28
50	50	+33	....	100	−27

Fusion Points of Silica-Titanium Oxide Mixtures

Silica, per cent	TiO_2, per cent	Cone of fusion	Silica, per cent	TiO_2, per cent	Cone of fusion
100	....	36	40	60	+30
90	10	33−34	30	70	29
80	20	29−30	20	80	29−30
70	30	26	10	90	−29
60	40	20	....	100	−27
50	50	27			

Bryce, using a mixture of Georgia kaolin and of Christy fire-clay with ruby rutile,[1] found that 5 per cent TiO_2 reduced the fusion-point of Georgia clay from cone 35 to cone 33, and 50 per cent TiO_2 reduced it to cone 17, while 25 per cent TiO_2 caused the fusion-point of Christy clay to drop from cone 33 to cone 23.

Kuechler,[2] in trying the effect of TiO_2 on Florida white clay and fire-clay, found that 5 per cent reduced the fusing-points 2 and 3 cones, respectively.

Searle [3] notes that 10 per cent TiO_2 added to silica reduces its fusion-point from cone 36 to cone 33–34, and that a eutectic is formed with 40 per cent TiO_2, 60 per cent SiO_2, whose fusion-point is cone 20.

He further states that 10 per cent TiO_2 added to alumina lowers its fusion-point from cone 42 to cone 37.

WATER IN CLAY [4]

Under this head may be included: 1. Mechanically combined water, and 2, chemically combined water.

Mechanically combined water.—This includes that which is held in the pores of the clay by capillarity. It may include water of plasticity, shrinkage water, and pore water.

Water of plasticity is that which is driven off when the clay is dried from a condition of maximum plasticity to 110° C.

Shrinkage water is that which passes off when the clay is dried from the condition of maximum plasticity, to the point where shrinkage practically ceases.

Pore water is that remaining in the pores of the clay after shrinkage has ceased, but is driven off at 110° C.

It will be seen from the above that the water of plasticity is equal to the sum of the shrinkage and pore water.

A high percentage of shrinkage water often indicates a fine-grained clay which may give a strong body when dry, while a high pore water content may be characteristic of a clay which when dried exhibits a weak porous structure.

Clay is very hygroscopic, and when thoroughly dried greedily absorbs moisture from the atmosphere, in fact, it may sometimes absorb as much as 10 per cent of its weight.[1]

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[1] Trans. Amer. Ceram. Soc., XII, p. 533, 1910.

[2] Jour. Amer. Ceram. Soc., IX, p. 105, 1926.

[3] Chemistry and Physics of clays, p. 368.

[4] See further under Shrinkage, Dehydration and Changes in Firing.

When water is added to a dry clay, the volume of the plastic mass exceeds the sum of the volumes of the clay and water, by from 1 to 5 per cent, and is thought to be due to mechanically enclosed air, or a slight swelling of the clay substance proper.[2]

Quantity of water in a clay.—The quantity of water in a clay may be expressed in several ways, as follows:

1. Ratio of pore water to shrinkage water. This for several types of clays has been given in the table below.

2.[3] Per cent shrinkage water in terms of true clay volume. This may be calculated by the formula

$$S = \frac{D(V_1 - V_2)\,100}{W}.$$

S = per cent shrinkage water in terms of true clay volume;
D = specific gravity of powdered clay;
V_1 = volume of clay briquette in wet state;
V_2 = volume of clay briquette in dry state;
W = weight of clay briquette in dry state.

Values for several types of clay are given in the table below.

3.[4] Per cent of total water in terms of true clay volume, calculated from the formula

$$T = \frac{D(W_1 - W)\,100}{W}.$$

T = per cent total water in terms of true clay volume;
D = specific gravity of powdered clay;
W_1 = weight of clay in wet state;
W = weight of clay in dry state;
$S - T$ = volume of pore water, and
$\frac{S - T}{T}$ = ratio pore to shrinkage water.

4. Per cent pore water in terms of true clay volume.

5. Per cent water in terms of dry clay weight.

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[1] Seger's Collected Writings, I, p. 214. In this connection see also Patten and Gallagher, Absorption of Vapors and Gases by Soils, Bureau of Soils, Bull. 51, 1908; and Bull. 50, 1908; also Lindsay and Wadleigh, Jour. Amer. Ceram. Soc., VIII p. 677, 1925.

[2] Bleininger, Colloid Symposium Monograph, II, p. 90, 1925.

[3] U. S. Bur. Standards, Tech. Pap. No. 79.

[4] Ibid.

Range of Different Kinds of Water in Several Types of Clay

	I	II	III	IV	V
Ball-clays	.64–1.10				
Crucible-clays	.56–1.36	69.5–132.5	37.2–84.8	40.5–55.1	
Glass pot-clays	.65–1.54	53.4–132.5	26.8–77.4	26.6–59.4	20.69–50.85
Plastic fire-clays for No. 1 fire-brick, Maryland	1.09–2.08				
Plastic fire-clays for No. 2 fire-brick, Maryland	1.13–4.15				
Stoneware-clay	.61–1.16	75.0– 90.6	37.1–55.6	34.0–45.0	

I Pore water, shrinkage water.
II. Per cent of water in terms of true clay volume.
III. Per cent of shrinkage water in terms of true clay volume.
IV. Per cent of pore water in terms of true clay volume.
V. Per cent of water in terms of dry clay weight.

Chemically combined water.—Chemically combined water, as its name indicates, is that which exists in the clay in chemical combination with other elements.

That which is combined in hydrous aluminum silicates passes off chiefly between 400° C. and 600° C., muscovite loses its water between 500° and 700° C., while hydrous iron oxides dehydrate between 150° and 350° C.[1]

Unless a clay contains considerable limonite or hydrous silica, the percentage of combined water is commonly about one-third the percentage of alumina found in the clay. In pure, or nearly pure kaolin, there is nearly 14 per cent, and other clays contain varying amounts, ranging from this down to 3 or 4 per cent, the latter being the quantity found in some very sandy clays. The loss of its combined water is accompanied by a slight but variable shrinkage in the clay, which reaches its maximum some time after all the volatile matters have been driven off.

In many clay analyses the chemically combined water is determined as loss on ignition, which is incorrect if the clay contains carbon dioxide, sulphur trioxide, or organic matter, all of which are driven off, in part at least, at a dull red. A properly made chemical analysis should also differentiate between water driven off below 100° C. and above 100° C.

CARBONACEOUS MATTER

Under this head is included all matter of carbonaceous character, most of which is of vegetable origin. Few sedimentary clays are entirely free from it, the material having become incorporated with the clay during its deposition. Although when first mixed with the clay it may have been more or less fresh, it has since then often undergone changes due to burial within the clay out of direct contact with the air, which have imparted to it an asphaltic or a coaly character.

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[1] See further under Dehydration, Chap. V.

Carbonaceous material may occur in clay in three different forms, namely:

1. Vegetable tissue, such as wood, leaves, stems, etc., in which form it is but slightly altered, and when of this character is commonly found in surface clays of recent origin. Organic matter of this character rarely affects the color of the raw clay and burns out easily, so that it causes but little trouble; then, too, it is usually present in but small amounts, rarely exceeding 1 per cent.

2. Carbonaceous matter of asphaltic or bituminous character. This burns readily at a low red heat, because of the highly combustible gases given off from it. It is found in some clays and in many shales, especially those associated with coal-seams, and in the shales which are worked may range anywhere from 0 to 10 per cent. If it increases above this the shales are not workable. Even 5 to 6 per cent causes much trouble in burning.

3. Hard, or coaly carbon, resembling anthracite. This burns slowly, and gives off few combustible gases.

Effects of carbon in clay.—Only the second and third of the groups mentioned need to be considered. The first alone causes trouble when it occurs in the form of sticks or thick roots and has to be screened out. It is, therefore, not included in what follows.

Carbonaceous matter often serves as a strong coloring agent of raw clays. If present in small amounts it tinges them gray or bluish gray,[1] while larger quantities cause a black coloration. Indeed, so strong may this be that it masks the effect of other coloring agents such as iron. In fact, two clays colored black might burn red and white, respectively, because one had much iron and the other none, and yet, owing to their black color, this could not be foretold with definiteness.

Asphaltic carbon, aside from its coloring action, often causes much trouble in burning, causing black cores, or even swelling and fusing of the brick. More than this, it may keep the iron in a ferrous condition and prevent the development of the best color-effects in the ware.

The reason for this is due to several causes:

Carbon has a strong affinity for oxygen, much stronger than that of iron, therefore as long as it remains in the clay it will monopolize the supply of oxygen and keep the iron in a ferrous condition, the form in which much of it is, in gray or black clays and shales. Now, in burning a clay, one of the aims of the clay-worker is to get the iron into a ferric condition, so as to fully develop its coloring properties and prevent other troubles. As long as any carbonaceous matter remains the oxidation of the iron is prevented or retarded, and consequently the carbon must be burned out.

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[1] See under Iron Oxide regarding another possible cause of bluish color.

The experiments of Orton and Griffin[1] have shown that between 800° and 900° C. is the best temperature interval for burning off the carbon, as below this the oxidation of it does not proceed as rapidly, and above this there is danger of vitrification beginning and the oxidation being stopped.

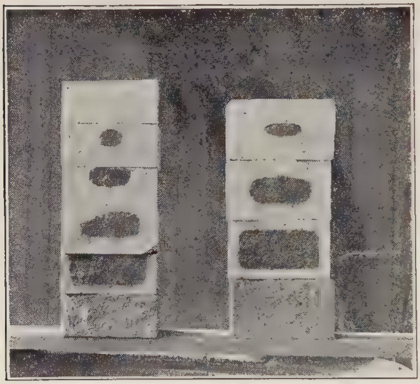

Fig. 45.—Changes in burning a black clay to a buff-colored brick. The lightest one was not removed from the kiln until the carbon was all burned off. (After Ries, N. J. Geol. Surv., Fin. Rept., VI, 1904.)

The method of procedure would therefore be to drive all moisture out of the clay first, then raise the heat as rapidly as possible to a temperature between 800° and 900° C., and hold it there until the ware no longer shows a black core denoting ferrous iron.

In order to burn off the carbon and oxidize the iron, air supplying oxygen must be drawn into the kiln during burning, for the gases of combustion from the fuel will supply none. Oxidation may be accelerated by increasing the amount of air entering the kiln and by reducing the density of the clay as much as possible.

In case this is not done, and the pores of the clay close up before all the carbon is burned off, it interferes with the expulsion of sulphur present which may result in a swelling of the clay. This may be even followed by complete fusion of the interior of the mass, caused by the formation of an easily fusible ferrous silicate. When the carbon is all burned off then the iron has a chance to oxidize.

If the clay contains much asphaltic carbon, then the oxidation must be carried on with as little air as possible, otherwise the heat generated by the burning hydrocarbons may be so intense as to vitrify the ware before the oxidation is completed.

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[1] Second Report of Committee on Technical Investigation, Indianapolis, 1905.

Since dense clays are more difficult to oxidize than porous ones, the process of manufacture may also influence the results, and in this connection it has been found that bricks made by the soft-mud process are most rapidly oxidized, followed by either the stiff-mud or dry-press (there being no difference between the two), and lastly by the semi-dry-press.

In some experiments made on Stourbridge fire-clay,[1] it was found that no change took place below 500° C., but that at 600° C. oxidation of the carbon had undoubtedly begun. With full-sized bricks the cores became blacker as the time at 600° C. is increased, but when the temperature approached 650° C., a white ring, which changed to yellow, followed the removal of the carbonaceous matter. At 750° C. there was a darkening in the shade of the interior, which was thought to be possibly due to a diffusion of the carbon, although reduction of the iron to a ferrous condition may also contribute to it. The black cores at this temperature were definitely replaced by persistent yellow areas and a more prolonged soaking at 750° C. would not remove them.

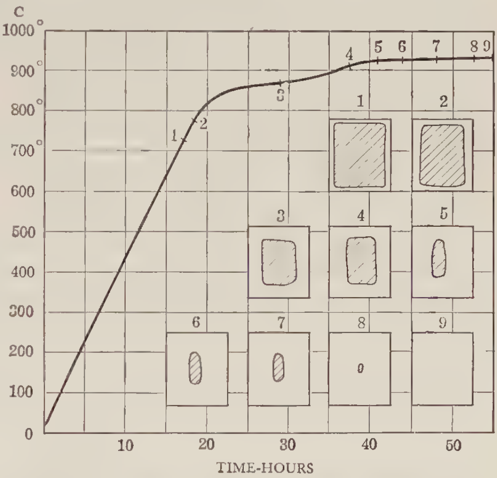

Fig. 46.—Oxidation chart of a carbonaceous shale paving block. (After Wilson, Univ. Wash., Eng. Exper. Sta., Bull. 18, 1923.)

Some other observers[2] have noted that carbon is burnt out completely by oxygen at 460° C. (850° F.).

Effect of water on black coring.—It is often stated by brickmakers that black cores are caused by the brick being set too wet. This is not strictly true, and the relation is but a very indirect one. While carbon burns off most rapidly between the temperatures of 800° and 900° C., still it also passes off somewhat at much lower temperatures. If now the brick is set wet it requires so much more heat in the early stages of firing to drive out or evaporate the water that other changes, such as the oxidation of the carbon, will be retarded, and brick begins to vitrify before the process is completed.

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[1] Theobald, L. S., and Green, A. T., Trans. Ceram. Soc. (Eng.), XXIV, p. 159, 1924–25.

[2] Bole and Jackson, Jour. Amer. Ceram. Soc., VII, p. 163, 1924.

Miscellaneous effects.[1]—Aside from the effects of carbonaceous matter mentioned above it may affect the plasticity of the clay especially if it is in colloidal form,[2] increase its water-absorbing capacity, and increase the shrinkage.

SULPHUR

Many clays contain at least a trace of sulphur, and some of them show appreciable quantities, but determinations of it are rarely made, unless the clay is to be employed for Portland cement manufacture. As can be seen from the experiments of Seger, and more especially Orton and Staley, it may cause serious trouble, and should always be determined in the analysis of a clay.

Sulphur might be present in a clay, as

1. Sulphate, such as gypsum ($CaSO_4 \cdot 2H_2O$), epsomite ($MgSO_4 \cdot 7H_2O$), or melanterite ($FeSO_4 \cdot 7H_2O$).
2. Sulphide, as pyrite (FeS_2), or marcasite (FeS_2).

In addition to sulphur being present in the raw clay, some of it may be of secondary nature due to oxides of sulphur given off by the fuel and being absorbed by the clay during firing, forming sulphates of iron, lime, or possibly other bases.

Jackson [3] states that Fe_2O_3 in clay will absorb sulphur from any source up to about 680° C.

From experiments on a Columbus black shale, running high in carbon, ferrous iron and sulphur, Orton and Staley [4] adopted the series of conclusions given below.

The shale contained an average of 2.997 per cent of total sulphur, expressed as the element, of which .76 per cent was contained in soluble sulphates and 2.235 in sulphides.

They conclude:

1. Both sulphates and sulphides experience rapid diminution by dissociation, in that portion of the burn up to 800° C., in those portions

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[1] Davis, Trans. Amer. Inst. Min. Engrs., LI, p. 455, 1915.

[2] For references on carbonaceous clays see Theobald and Green, Trans. Eng. Ceram. Soc., XXIV, p. 159, 1924–25; Keele, Brick, LV, p. 45, 1919; Stull & Hursh, Ill. Geol. Surv., Cooperating Coal Mining Series, Bull. 18, 1917; Bole and Jackson, Jour. Amer. Ceram. Soc., VII, p. 163–174, 1924; Mellor, J. W., Trans. Ceram. Soc. (Eng.), XVI, p. 259, 1917.

[3] Jour. Amer. Ceram. Soc., VII, p. 537.

[4] Third Report of Committee on Technical Investigation, Nat. Brick Makers' Assoc., Indianpolis, 1908.

of the ware which get air freely. This loss of sulphur may amount to two-thirds or three-fourths of the amount originally present.

2. Both sulphates and sulphides experience a further slow diminution by dissociation or oxidation, beginning at 800° C., and continuing as long as the clay structure remains porous and permeable to air. The loss of sulphur may amount to 90 per cent or more of the initial sulphur content at the end of the period, but it proceeds increasingly slowly, and would probably never become complete.

3. In the interior portions of the clay, to which air cannot readily penetrate, the loss of sulphur may be less, and if there are any bases, such as FeO, CaO or MgO present, with which the sulphur may combine, the sulphur is not likely to be expelled.

4. Carbon, even in small quantities, interferes strongly with the expulsion of sulphur, which does not pass off to any extent until after the carbon goes. The clay may therefore have become too dense by that time for the oxidation of the sulphur to proceed, so that the carbon has virtually prevented its escape.

5. Sulphur retained in the clay in any form and from any cause is not likely to cause physical disturbances in the clay until a fairly complete degree of vitrification is reached.

6. When a clay reaches a dense vitrified condition it proceeds normally, after a longer or shorter interval, to become less dense, by reason of the development of multitudes of minute vesicles in the viscous body; this process is progressive and in the end the body becomes spongy and worthless.

7. The length of this period of dense vitrification is much shortened, and in some cases practically abolished, by the presence of sulphur compounds, which break down and evolve gases copiously, producing a prematurely spongy body.

8. The cause of this gas evolution is chiefly the dissociation of sulphides and sulphates by silicic acid, which becomes increasingly active as the temperature rises, and appropriates the bases formerly combined with the sulphur.

9. In clays of low sulphur content, and of favorable structure for oxidation, the amount of sulphur left in the clay at vitrification is very small. Hence the period of good structure is long, the vesicular structure develops slowly, and the clay is said to stand overfiring well.

10. In clays of high sulphur content, or of dense structure unfavorable for oxidation, or of high content of iron and carbon, the escape of the sulphur is prevented, the clay has a very narrow period of usefulness, or none at all, and the vesicular structure becomes enormously exaggerated.

11. While this premature and exaggerated swelling from sulphur may in bad cases occur in well oxidized clays, it is practically certain to occur where clays containing a partly oxidized core are allowed to reach the vitrification period.

12. This breaking down of sulphur compounds by silicic acid is the chief or common cause of the premature swelling of black colored clays, and the occasional cause of sudden and severe swelling of properly oxidized clay wares.

13. The proper way to avoid the effects of sulphur in vitrifying clay bodies is to apply a deliberate and complete oxidation treatment while the clay remains porous. This will rid the clay of the greater part of the sulphur, and will prevent sudden or premature slagging of the clay by ferrous oxide, if it is true that ferrous oxide has such a tendency, and will thus avoid, so far as possible, the conditions which favor swelling. Clays which still give trouble from swelling after treatment must be regarded as bad clays.

Ferrous sulphide cannot be broken up by heat alone, but only by roasting in air, or interaction with silicic acid, for according to Seger,[1] silicic acid at high temperatures has the power of displacing all other common acids, and combining with their bases to form silicates. It thus has the power to replace sulphuric acid, and the sulphur of sulphides. He found that a bisilicate glass mixture, saturated with sulphates, showed 4 per cent sulphuric acid, while the same glass with one more molecule of silica added and melted at the same temperature and under same conditions contained but 2 per cent sulphuric acid. Applying this to clay he reasoned that in raising the temperature of burning, the fusing matrix of a clay becomes more siliceous, resulting in the expulsion of sulphur.

The diagram, Fig. 47, shows the rate of expulsion from the Columbus shale tested by Orton and Staley.[2]

Jackson has recently presented a most interesting series of articles on this subject,[3] in which he emphasizes certain points and detailed laboratory and plant experiments.

He notes, as already recognized, that when pyrite is heated, a portion of the sulphur is driven off, the FeS_2 burning to FeS and SO_2. This may take place at not above 500° C., but all of the sulphur is not gotten rid of until 925° C.

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[1] Collected Writings (Translation), II, p. 646, 1902

[2] l. c.

[3] Jour. Amer. Ceram. Soc., VII, pp. 163, 223, 427, 532, 634, 656; see also Mellor, Trans. Eng. Ceram. Soc., VI, p. 142, 1907, and VII, p. 112, 1908.

The FeS may by oxidation change in several ways as follows:

$$4FeS + 7O_2 = 2Fe_2O_3 + 4SO_2;$$

$$FeS + 2O_2 = FeSO_4;$$

$$2FeS + 5O_2 + SO_2 = Fe_2(SO_4)_3.$$

If ferric sulphate is formed, the decomposition of this is mostly between 560° and 775° C.

If evolution of SO_2 or SO_3 due to oxidation of FeS_2 takes place, much of this may be absorbed by impurities in the clay to form sulphates.

If the sulphur remains in the clay it may form a ferrous-sulphosilicate [1] which is not easily decomposed by the heat, but when decomposition begins it may occur suddenly and swell the ware, if there is no chance for the evolved gases to escape.

On this point Jackson appears to differ with Orton and Staley, and Seger, who assumed that the silica displaced sulphur and joined the iron.

If oxygen cannot get into the ware, the iron remains in a ferrous state and forms a black core.

Since the sulphur causing trouble in ceramic work may sometimes be derived in appreciable quantity from the coal, the composition of the fuel should be carefully considered.[2]

Sulphur from fuel is carried into the kiln chiefly in the form of sulphur dioxide, and at first will be oxidized and absorbed by the ware if sulphates of any bases are present, such as iron, alumina, lime, magnesia and potash.

One fact brought out by Jackson's experiments was that increasing the amount of sulphur in the kiln atmosphere did not cause a corresponding increase in the absorption of sulphur by the ware, in fact a large proportion of the maximum absorption occurred in a kiln atmosphere of very low sulphur content. The greatest absorption of sulphur took place at about 496° C. The time of firing seemed to exert little influence.

The author concluded that sulphur combines with the different bases according to the nature of the compound in which they exist in the clay and also to the temperature. Carbonates are the most easily attacked, and silicates less so. Water vapor is the intermediate agent needed for the formation of objectionable sulphur compounds.

The preventive measures are thorough drying of the ware, maintenance of a good draft during water smoking, and use of clays free from carbonates of iron, lime and magnesia.

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[1] Jackson, Jour. Amer. Ceram. Soc., VII, p. 537, 1924.

[2] See C. W. Parmelee, Effect of Sulphur in Coal used in Ceramic Industries, Amer. Inst. Min. Engrs., Trans., LXIII, p. 727, 1920.

Summarizing Jackson's work the following points may be noted:

Much of the volatile sulphur in the coal may be absorbed by the ware up to 760° C., and in four ways: (*a*) SO_2 is absorbed by surface moisture up to 100° C., after which the H_2SO_3 is decomposed; (*b*) SO_3 is similarly absorbed up to 100° C., but the H_2SO_4 is not decomposed below 260° C.; (*c*) $Fe_2(SO_4)_3$ is formed by absorbed acid solutions or kiln gases; (*d*) sulphur is locked up in an insoluble form, possibly sulphosilicate.

Sulphur is evolved from the kiln in the following ways: (*a*) Sulphur gases not absorbed by the ware; (*b*) SO_2 from SO_3 breaking up at 100° C.; (*c*) SO_3 from H_2SO_4 at about 260° C.; (*d*) decomposition of pyrite, etc., beginning at about 426° C.; (*e*) decomposition of $Fe_2(SO_4)_3$, mostly between 560° C. and 775° C.; (*f*) decomposition of ferrous sulphosilicate, probably beginning about 704° C. The evolution of the sulphur may be temporarily retarded by igniting carbon in the kiln, which would tend to retard oxidation of pyrite. A core may be formed if pyrite is burned out on the surface only. Too rapid firing forms a different core.

PHOSPHORIC ACID

Phosphoric acid is a substance that is rarely determined in clays, though it is not unlikely to have a wide distribution. It might be present as an ingredient of either amorphous or crystalline phosphate of lime, or of vivianite, the phosphate of iron, or perhaps even other phosphates.

In West Virginia it was found in all the clays examined in the laboratory of the Geological Survey.[1] About one-quarter of the clays showed only a trace, but in the others it varied from .04 to 1.09 per cent, with an average of .316 per cent.

Whether such small amounts exert any recognizable effect in burning is not known, but, C. W. Parmelee [2] states that the presence of phosphoric acid in sufficient amount gives translucency to the ware, improves the color, and acts as a flux and vitrifying agent.

With a slight increase in silica, the fusibility is increased, and the addition of lime or feldspar in small quantities also made the mixture more fusible.

Thus a mixture of the formula $Al_2O_3 \cdot .56\ SiO_2 \cdot .7\ P_2O_5$ showed marked translucency, but stood at cone 13. One with $Al_2O_3 \cdot 2.8\ SiO_2 \cdot .7\ P_2O_5$ was half over, while a third with $.3\ K_2O \cdot Al_2O_3 \cdot 2.8\ SiO_2 \cdot .7 P_2O_5$ was melted at the same cone.

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[1] W. Va. Geol. Surv., III, p. 21, 1906.

[2] Action of Phosphoric Acid in Body Mixtures, Trans. Amer. Ceram. Soc., VIII, p. 238, 1906.

VANADIUM

Although this element is not common in clays, small quantities are not uncommon and may be the cause of discoloration. In Germany vanadates have been found in clays associated with the lignites, and also some fire-clays.[1] Clays containing soluble vanadates, if not fired at a sufficiently high temperature, will show on the surface of the ware a green discoloration which, although it can be washed off with water, will continue to return as long as any of the salt is left in the brick.

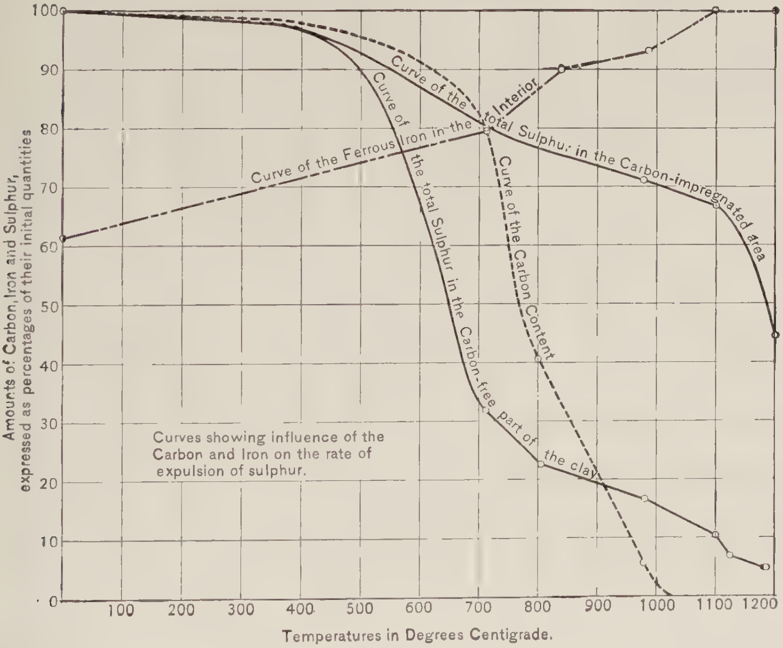

FIG. 47.—Curves showing influence of the carbon and iron on the rate of expulsion of sulphur. (After Orton and Staley.)

O. Kallauner and I. Hruda [2] after pointing out that Seger noted that KVO_3 often causes scumming and yellow discoloration on bricks, quote their experiments to the effect that V_2O_3 in small amounts does not affect the fusibility of the clay, but that 20 per cent reduced the fusion-point of kaolin from cone 35 to 30, and 40 per cent reduced it to cone 15. V_2O_3 caused yellow discoloration in amounts as small as .1 per cent, and as little as .001 per cent might cause scumming. This they say may be reduced by the addition of barium or lime compounds, or by reducing fire.

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[1] Seger, Ges. Schrift., p. 301; also Tonindus. Zeit., No. 46, p. 53, 1877.

[2] Sprechsaal, XLV, p. 333 and 345, 1922.

SOLUBLE SALTS [1]

It is a well-known fact that many clays contain at least a small percentage of water-soluble compounds, which may be brought to the surface on drying, remaining there as a coating, usually white in color.

These white coatings may appear on the ware during the drying, burning, or even after setting in the wall.

It has been suggested by Parmelee,[2] that the term *efflorescence* be used to designate those accumulations of soluble salts upon the surface, which have been brought there in solution, and deposited when the water evaporates. The term *scum* he recommends be restricted to those deposits of soluble salts formed by the action of gases upon the wares during drying and burning.

Sources of soluble salts in clay.—It has been pointed out in Chapter I (Origin of Clay) that in the decomposition of mineral grains clay soluble compounds are often formed.

Pyrite or more particularly marcasite, will oxidize to iron sulphate, which when brought to the surface by water, may be deposited there as a yellowish or brownish efflorescence. There is in addition an indirect trouble, in that sulphuric acid is set free in the decomposition of the iron sulphide, and may attack carbonates of lime, magnesia or iron in the clay, and form sulphates.

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[1] For additional information on this topic see the following references: Ashley, U. S. Bur. Stand., Tech. Pap. No. 25. p. 96; Bleininger, Trans. Amer. Ceram. Soc., XV, p. 523, 1913; Coates, Trans. Amer. Ceram. Soc., XVI, p. 162, 1914; Collin, Can. Dept. Mines, Mines Branch, Investigations 1925, No. 672, p. 9, 1926; Curry, Jour. Amer. Ceram. Soc., IX, p. 392, 1926; Gates, Jour. Amer. Ceram. Soc., III. p. 313, 1920; Gerlach, Brickbuilder, 1898, p. 59; Guenther, Baumaterialienkunde, I, p. 386, 1896; Haegerman, Tonindus. Zeit., L, p. 237, 1926; Hill, Bull. Amer, Ceram. Soc., I, p. 51, 1922; Jones, Trans. Amer. Ceram. Soc., VIII, p. 369, 1906; Lovejoy, Trans. Amer. Ceram. Soc., VIII, p. 255, 1906; Mäckler, Tonindus. Zeit., No. 43, 1904; Mellor, Clay and Potteries Industries, p. 53; Parmelee, Jour. Amer. Ceram. Soc., V, p. 543, 1922; Parmelee, Brick, LXI, p. 249, 1922; Seger, Collected Writings, I, pp. 213, 376, 369, 381; Sembach, Ber. deut. Keram. Ges., V, p. 225, 1925; Williams, Trans. Amer. Ceram. Soc., XVII, p. 764, 1915, and XVIII, p. 271, 1916.

[2] Jour. Amer. Ceram. Soc. V, p. 543, 1922.

Parmelee suggests using such a clay promptly, or else to weather it long enough to permit the complete change and leaching of the sulphides. This may not help, however, if more sulphates are formed.

As an illustration of the development of soluble salts in weathering, Ries [1] gives the case of a clay containing pyrite, which showed .2 per cent soluble salts when mined, and .87 per cent after weathering.

It is possible that some of the soluble matter may be due to portions of the clay particles going into solution as a result of long contact with water.

In some cases soluble sulphates may be even introduced into the clay by the water used for tempering, for distilled water is the only kind that is free from soluble salts. All well and spring waters contain some at least, and if these flow or drain from clays or rocks containing any pyrite they are almost sure to contain soluble salts. Those flowing from lime rocks are usually " hard," on account of the lime carbonate which they contain. Still another source of soluble salts in raw clay lies in some of the artificial coloring materials which are sometimes used.

Character of soluble salts.—According to Parmelee, soluble salts include hydrated silicic acid, aluminum salts, probably mostly sulphate, sulphates of iron, lime, magnesia, soda and potash, and also sodium chloride. Of these the sulphates of lime and magnesia are commonly regarded as the most troublesome.[2]

Amount of soluble salts in clay.—A number of determinations of soluble salts have been made by different investigators.

Mellor [3] gives .015 per cent for English china-clay and .4 per cent for ball-clay. In the latter he states they are chiefly soluble silicic acid and soluble silicates of alkalies and alkaline earths, with about 1–2 per cent of alkaline chlorides, and about 20 per cent sulphates. For New Jersey clays, Ries [4] records, zero to 1.49 per cent, and for Texas,[5] .05 − 1.21 per cent. Grout, for West Virginia,[6] reports from .05 − 1.21 per cent.

Amount of soluble salts causing trouble.—It is not definitely known how much soluble matter is permissible in a clay without danger of its forming a white coating, but it is probable that less than .1 per cent may cause trouble. Searle[1] says that as little as .01 per cent of sulphates have been known to spoil a facing-brick, and quotes Mäckler as stating that the amount of scum on the ware bears a definite relation to the amount of magnesium and sodium sulphates, but not to the total soluble salts. In a series of fifty bricks which Mäckler[2] examined he found that the sum of the sulphates of lime, magnesia and alkalies varied from .0134 per cent to .7668 per cent.

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[1] Univ. of Texas, Bull. 102.

[2] Grimsley and Grout (W. Va. Geol. Surv., III) in their work on the W. Va. clays found that some of the soluble salts were unexpectedly high in Al_2O_3 and SiO_2, and showed no sulphates.

[3] Clay and Pottery Industries, p. 56.

[4] N. J. Geol. Surv., XI, p. 76, 1905.

[5] Univ. of Texas, Bull. 102, p. 45.

[6] W. Va. Geol. Surv., III, p. 26, 1905.

Soluble salts developed during manufacture.—The term *dryer-white* is applied to a coating of soluble salts which forms on the ware in the dryer or dry-house. If in the nature of efflorescence it may be due to soluble salts in the clay or in the water used for mixing. The more soluble the compounds, and the finer their texture, the easier they go into solution and the more abundant the efflorescence. Finer-grained clays dry more slowly, and this may encourage the movement of soluble salts to the surface, because the water moves slowly and is longer in contact with the particles.

The scum formed on the ware in drying may be due to waste gases from the kiln which carry oxides of sulphur. These coming in contact with carbonates in the clay in the presence of moisture convert them into sulphates (see under Sulphur.) *Kiln white* is a name applied to surface accumulations of soluble salts formed during burning.

If in the nature of efflorescence, it may come from soluble salts in the ware, which have been brought to the surface of the latter, if not in the dryer, then during the early stages of burning.

If the coating is scum, it may be due to oxides of sulphur in the fuel, acting in the same manner as mentioned under dryer white. Parmelee[3] points out, however, that if the temperature is sufficiently high the " acid passes through the kiln with little or no effect on the ware." In the event of the ware being fired sufficiently hard, the soluble salts may be fixed by fluxing with other ingredients of the clay.

This is brought out by the following determinations made by the author on five samples of bricks made from a limy clay and representing different degrees of firing.[4]

SOLUBLE SALTS IN FIRED BRICK

		Per cent
A	Softest burn	4.50
B		2.20
C		1.42
D		1.23
E	Hardest burn	1.03

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[1] Clayworkers' Handbook, p. 335.

[2] Tonindus. Zeit., No. 43, 1904.

[3] l. c.

[4] Ries, Wis. Geol. Surv., Bull. XV, p. 21, 1906.

With reducing atmosphere in the kiln sulphites may form instead of sulphates and these are easily decomposed.

The name *wall white, wall saltpeter* or *wall niter*, is applied to white coatings of soluble salts appearing on brick walls. It sometimes appears on bricks piled up in the yard on ashes or cinders, being drawn up from these by moisture.

In other cases it may come from the brick itself, from mortar especially if it contains too much lime, from gypsum in Portland cement mortar, from mortar colors, or even salt if the latter is used in mortar during freezing weather.

Porous bricks are apt to give more trouble than dense-burned ones. Disintegration of brick work is sometimes due to soluble salts crystallizing in the pores.

Disintegration of brick, concrete or building stone is sometimes noticed in dry climates, where the soil contains much soluble mineral matter, which is drawn up by evaporating moisture.

In some instances the bricks become covered with a yellow or green stain, which is caused either by the growth of vegetable matter on the surface of the ware, or by soluble compounds of vanadium,[1] although another writer, Hill, claims that the yellow-green stain developed on some clay products is due to iron.[2]

Prevention of soluble salts.—The methods of prevention that have been suggested for dryer-white and kiln-white are:

1. Use of the clay in its unweathered condition, or before the soluble salts have time to form.
2. Use of the clay in a thoroughly weathered condition, thus permitting removal of soluble salts by leaching.
3. Change the soluble salts to a harmless form by precipitation with barium compounds.
4. Prevention of concentration of salts on surface of brick by rapid drying.
5. Removal of scum in the kiln by using a reducing flame.
6. Coating of the brick with some combustible substance, as wheat flour or coal-tar, which burns away with a strong reducing action and removes the soluble salts.

Referring in more detail to 3, it may be explained that the substance commonly added is either barium chloride or barium carbonate. When barium salts come in contact with soluble sulphates, barium sulphate is formed, a combination which is insoluble in water. This is expressed by the following chemical reactions if barium carbonate is used:

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[1] Seger's Collected Writings, p. 381.

[2] Bull., Amer. Ceram. Soc., I, p. 51, 1922.

$$CaSO_4 + BaCO_3 = CaCO_3 + BaSO_4.$$

We thus see that we get compounds which are less soluble than the original ones. If soluble sodium compounds are present, the addition of barium carbonate will form sodium carbonate, but since this is easily soluble in water it can be washed off without much trouble.

Barium chloride, because of its greater solubility and easier distribution through the clay, may be used in place of a part of the barium carbonate. An excess of it might cause efflorescence. Barium fluoride, which is intermediate in solubility between the carbonate and chloride, has also been suggested, as has been barium hydroxide.[1]

Since, in drying molded-clay objects, the evaporation is greatest from the edges and corners of the ware, the incrustations may be heaviest at these points, but the more rapidly the water is evaporated the less will be the quantity of soluble salts deposited on the surface. Incrustations which appear during drying are found more commonly on bricks made from very plastic clays, which, owing to their density, do not allow the water to evaporate quickly.

Remedy for wall-white.—This is more difficult, but consists primarily in preventing entrance of moisture to the walls. It is suggested to make the walls as impervious as possible by the use of well-burned brick, and proper drainage and waterproofing of the foundations. If the efflorescence appears, the walls may be painted so as to cover the efflorescence, but it may then peel off in damp spots. A coat of paraffine or linseed oil will conceal the white coating somewhat, but also darken the brick. They should also be made waterproof if possible.

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[1] Gates, Jour. Amer. Ceram. Soc., III, p. 313, 1920.

CHAPTER IV

PHYSICAL PROPERTIES OF CLAY

Introductory.—Under Physical Properties there are included plasticity, texture, green strength, shrinkage, volume, porosity, specific gravity, color, slaking, permeability, capillarity, absorption, and fusibility.

PLASTICITY

Definition.—Plasticity is probably by far the most important property of clay, lacking which it would be of comparatively little value for the manufacture of clay products. Seger[1] has defined it as the property which solid bodies show of absorbing and holding a liquid in their pores, and forming a mass which can be pressed or kneaded into any desired shape, which it retains when the pressure ceases, and, on the withdrawal of the water,[2] changes to a hard mass. The term hard of course refers to its hardness as compared with its wet condition, for some air-dried clays are rather soft.

This is a somewhat narrow interpretation of the property of plasticity, and one which would practically exclude anything except very plastic clays.

A broader conception, and probably a more satisfactory one to the physicist, would be to define plasticity as the property which many bodies possess of changing form under pressure, without rupturing, which form they retain when the pressure ceases, it being understood that the amount of pressure required, and the degree of deformation possible, will vary with the material.

Definitions similar to Seger's have also been suggested by Grout[3] and Searle,[4] but the latter likens it to the malleability of metals, although remarking that clays are unique in that the plasticity is destroyed on loss of water.

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[1] Beziehungen zwischen Feuerfestigkeit und Plasticität der Tone.—Tonindustrie-Zeitung, 1890, p. 201; Collected Writings, I, p. 533.

[2] By evaporation.

[3] Jour. Amer. Chem. Soc., XXVI, p. 1037, 1905.

[4] Chemistry and Physics of Clays and other Ceramic Materials.

Bingham[1] says plasticity is a complex property, and that it involves at least two factors, viz.: (1) A definite shearing stress, or the yield value, and (2) mobility which is determined by measuring the volume flow of the clay in a given time, under varying pressures, through a capillary tube.

According to this, the line of demarcation between a viscous suspension and a plastic substance is that in the former the line of the pressure-flow curve passes through the origin, but in the latter intersects the axis at a definite pressure value. The slope of the linear-pressure flow curve is a function of the mobility and the intercept of the yield value.

J. W. Mellor[2] defines plasticity as "the property which enables a clay to change its shape without cracking when it is subjected to a deforming stress."

According to him it is affected by two factors: 1. The internal friction which can be otherwise represented as the resistance which the clay offers to changing its shape. 2. The cohesion, represented by the amount of deformation which the clay can suffer without cracking.

Plasticity might not be regarded as a property of clays alone, for, as pointed out by B. Zschokke[3] in connection with his study of the methods of testing it, other bodies, such as lead and wax, are plastic in their natural condition at ordinary temperatures, while copper, steel, and glass are plastic at higher temperatures.

Others, like clay and some mineral aggregates, are plastic only when wet, but even then vary greatly in their plasticity.

Some writers on clay, in attempting to give examples of plastic and non-plastic bodies, have sought to compare clay and sand, stating that the latter, even when fine-grained and wet, shows no plasticity; and, while it is true that a very fine-grained wet sand, or a finely ground mass of quartz, does not under pressure show the same amount of deformability without rupture as clay, still it shows some,[4] and the question may be asked whether both are not classifiable as plastic bodies, the one but slightly plastic and the other highly so. It is indeed possible to get a series of samples showing a complete gradation from a highly plastic clay to a but slightly plastic ground quartz. The latter will moreover hold its shape when dry, even though it will stand practically no handling without breaking.

Instead, therefore, of intimating that plasticity when wet is a property peculiar to clay, it would perhaps seem more correct to state that this property is highly developed in clays as compared with other earthy and sandy materials of very fine grain.

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[1] Proc. Amer. Soc. Test. Mat., 1919–1920.

[2] Trans. Ceram. Soc., (Eng.) XXI, p. 91, 1921.

[3] Tonindustrie-Zeitung, No. 120, p. 1658, 1905; and Baumaterialienkunde, 1902, No. 24, 25–26; 1903, Nos. 1–2, 3–4, and 5–6.

[4] See G. P. Merrill, Non-metallic Minerals, p. 221.

An important character, closely dependent on the degree of plasticity exhibited by finely textured mineral aggregates, is the assumption of a more or less hard condition when dry, the degree of hardness increasing usually with the plasticity.

Hardening on exposure to heat is not necessarily a function of plasticity, but is due to the particles softening by fusion and becoming welded together. In those highly plastic mineral aggregates (our most plastic clays) this hardening begins to take place at a comparatively low temperature, because the particles are very fine-grained and come into the closest contact, thereby facilitating heat reactions; while, in the coarser-grained ones, the particles are not only more or less separated by interspaces, but there are more quartzose grains, which of themselves are refractory, and therefore heat reactions occur at higher temperatures, or else, if any fusion occurs at a lower heat, it is insufficient to bind the mass together into an impervious body.

Cause of plasticity in clay.—Scientists have for a long time sought to explain the cause of this most interesting physical property, and, while many theories have been advanced, none are wholly satisfactory.

The theories proposed are: Water of hydration, Texture, Plate, Interlocking grain, Ball, Colloid, Molecular attraction, etc.

Water of hydration theory.—Several of the earlier writers including Vogt,[1] Arons,[2] Bischof,[3] Seger,[4] as well as others have expressed the view that the hydrated aluminum silicates in the clay, were at least one, if not the sole cause of plasticity. This was based on the assumption that the dehydration of the kaolinite and the loss of plasticity, were coincident, and furthermore that kaolinite formed the basis of all clays, a view now known to be incorrect (see Origin of Clay.).

The combined water, however, does not bear any direct relation to the plasticity, for two clays having exactly the same amount, may differ greatly in their plastic qualities, and some very plastic clays contain little hydrated silicate of alumina.[5] It has also been shown [6] that all the combined water of the clay is not a part of the clay base in the sense of water of hydration, and that the clay has no definite dehydration temperature.

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[1] Tonindus.-Zeit., 1893, p. 140, and Comptes rend., Acad. Sci. Paris, CX, p. 1199, 1890.

[2] Dammer, Chemische Technologie der Neuzeit, I, 1910.

[3] Die feuertesten Thone.

[4] Collected Writings, I, p. 69.

[5] Ries, Md. Geol. Surv., IV, p. 248, 1902. Seaman (Chem. Centralbl., 1890, I) describes a highly plastic clay which contains practically no Al_2O_3, but shows, Ign., 7.95; ZnO, 54.06; SiO_2, 35.29; CaO, 1.80; Al_2O_3, 1.64.

[6] Montgomery and Brown, U. S. Bur. Stand., Tech. Pap. No. 21, 1913.

Montgomery and Brown, for example, assert that dehydration does not necessarily completely destroy plasticity, while Rohland [1] contends that it is lost at the temperature at which combined water begins to be evolved, or about 590° C.

In the experiments of the former [2] it was found that surface clays examined lost their plasticity at about 400° C., ball-clays at 450° C., kaolins at 500°–600° C., the more plastic ones being affected more than the less plastic; No. 2 fire-clays at 600°–750° C., and some shales at 750°–800° C.

Texture theory.—Among the theories advanced to explain the cause of plasticity is that of fineness of grain. Whitney, for example, in studying soils, has designated as clay all those portions which were under .005 mm. in diameter.[3]

While it is true that the clayey particles of clays consist of grains of all sizes below the limits mentioned above, still plasticity cannot be explained on this ground alone. Very finely ground quartz, feldspar or mica are slightly plastic, but not nearly as much so as most clays. Moreover, the finest-grained clays are not always the most plastic ones. Wheeler [4] has noted that samples of quartz and limestone ground sufficiently fine to pass a 200-mesh sieve felt plastic when wet, but fell to pieces when dry, and the same results were obtained by Orton [5] with glass ground to exceeding fineness. When we recollect, however, that clay particles are smaller than 0.0001 mm., 0.02 in. (0.508 mm.) is not sufficiently fine grinding for testing the accuracy of the theory. That fineness no doubt exerts some influence on plasticity is evidenced by the fact that fairly plastic clays can often be rendered more plastic by fine grinding, and the addition of sand is said by Beyer and Williams to injure plasticity directly as the diameter of the grains increases.[6]

On the other hand Wheeler found that finely ground gypsum and brucite had considerable binding power and plasticity, but in this case the plasticity was not ascribed to fineness alone.

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[1] Silicat. Zeit., II, p. 30, 1914.

[2] Brown, G. H., and Montgomery, E. T., U. S. Bur. Stand., Tech. Pap. No. 21, p. 16.

[3] The Mechanical Analysis of Soils, Dept. of Agric., Bur. of Soils, Bull. 4, p. 15, 1896.

[4] Mo. Geol. Surv., XI, p. 102, 1896.

[5] Brick, Vol. XIV, p. 216.

[6] Ia. Geol. Surv., XIV, p. 86, 1904; also Douda, Jour. Amer. Ceram. Soc., III, p. 885, 1920.

In this connection we may point to the researches of Daubrée, who claimed that feldspar, ground wet, gradually became plastic if allowed to stand, but that dry-ground feldspar lacked plasticity, and from this Olchewsky has reasoned that it is prolonged contact of the mineral grains with water during their sedimentation that develops plastic qualities in the mass.[1]

These differences of opinion as pointed out by Davis [2] may be due to the fact that the several authors have not the same conception of what constitutes a plastic mass or where plasticity ends.

Other observers as Grimsley and Grout,[3] Atterberg,[4] Rohland,[5] and Daubrée,[6] have commented on the increase in plasticity which is caused by grinding.

Plate theory.—Johnson and Blake [7] advanced the theory that most plastic clays seem to be composed largely of small transparent plates, which were bunched together. They state:

> "We have examined microscopically twenty specimens of kaolins, pipe- and fire-clays. . . . In them all is found a greater or less proportion of transparent plates, and in most of them the plates are abundant, evidently constituting the bulk of the substance.
>
> "The plasticity of a clay is a physical character, and appears to have close connection with the fineness of the particles. The kaolinite of Summit Hill, consisting of crystal plates averaging 0.003 of an inch in diameter, is destitute of this quality. The nearly pure kaolinite from Richmond, Va., occurring mostly in bundles of much smaller dimensions, the largest being but 0.001 of an inch in diameter, is scarcely plastic. . . . The more finely divided fire-clay from Long Island is more 'fat,' while the Bodenmais porcelain earth, and other clays in which the bundles are absent and the plates are extremely small, are highly plastic."

Other investigators appear to have attributed the cause of the plasticity to these plates, for this same view was advanced in 1878 by Biedermann and Herzfeld,[8] and in this country a similar view was held by Cook,[9] who considered the plasticity to be due to the plates of kaolinite. He noted the bunched character of these in some clays, and pointed out that attrition broke up these bunches and increased the plasticity.

Haworth,[10] in examining the Missouri clays, found the most plastic clays to be composed of minute scales, and Wheeler[1] sought to prove this point experimentally by finely grinding minerals possessing a plate-like structure. Calcite and gypsum when finely ground were found to develop good plasticity when mixed with water, and to have tensile strengths when air-dried of 100 and 350 lbs. per sq. in. respectively. Talc and pyrophyllite were likewise plastic when finely ground and mixed with water, but developed little strength when dry.

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[1] See also Linder, E. T.; Tonindustrie-Zeitung, XXXVI p. 382.

[2] Trans. Amer. Inst. Min. Engrs., LI, p. 455, 1915.

[3] W. Va. Geol. Surv., III, p. 46, 1905.

[4] Zeitschr. f. angew. Chem., XXIV, No. 20, 1911.

[5] Die Tone, Vienna, 1909.

[6] Referred to by A. S. Cushman, Trans. Amer. Soc., VI, p. 66, 1904.

[7] Amer. Jour. Sci. (2), p. 351, 1876.

[8] Bischof, Die Feuerfesten Thone, p. 23; also Hussak, Sprechsaal, 1889, p. 135.

[9] N. J. Geol. Surv., Report on Clays, 1878, p. 287.

[10] Mo. Geol. Surv., Vol. XI, p. 104, 1896.

LeChatelier[2] and Atterberg[3] also leaned towards the plate theory.

It must be admitted that a mass of very small platy grains, slipping over each other and separated by films of water, would no doubt exhibit both mobility and cohesion,[4] and there is some evidence bearing on it.

Thus, R. T. Stull[5] found that mica after grinding showed a "surprising increase in plasticity," while Ries[6] has described a clay from Texas which was sufficiently plastic to mold, but which analyzed 98 per cent dolomite, and under the microscope was seen to be made up of little rhombs about 0.008 mm. in diameter. Another interesting case would be that of bentonite, which when pure is made up largely of microscopic plates of the mineral montmorillonite, and which may show appreciable plasticity. Lastly, attention might be called to the comment of Cook, who claimed that the New Jersey fire-clays showed bunches of small plates, which when separated by grinding increased the plasticity of the clay.[7]

Interlocking-grain theory.—Olchewsky[8] was probably the first to suggest that the plasticity and cohesion of a clay were dependent on the interlocking of the clay particles and kaolinite plates, and in this connection used the briquette method of testing the plasticity, or rather obtaining a numerical expression for it, by determining the tensile strength of the air-dried clay.

Still later two Russian investigators, U. Aleksiejew and P. A. Cremiatschenski, in studying the Russian clays[9] have come to the conclusion that plasticity is due not only to the interlocking of the clay particles, but varies also with the fineness of the grain, the extreme coarse and fine ones both having less plasticity.

If the tensile strength of a clay depends on the degree of interlocking of the clay particles, then the tensile strength should afford us a means of expressing numerically the plasticity of the clay. It appears, however, that there is no such constant relation between these two properties.

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[1] Ibid., p. 106, 1896.

[2] Van Bemmelen's Gedenkboek, p. 163.

[3] Zeitschr. für angew. Chem., XXIV, May 19, 1911.

[4] See description of Montmorillonite.

[5] Trans. Amer. Ceram. Soc., IV, p. 257, 1902.

[6] Amer. Jour. Sci., XLIV (4), p. 316, 1917.

[7] Clays of New Jersey, N. J. Geol. Surv., 1878.

[8] Töpf. u. Zieg. Zeit., No. 29, 1882.

[9] Zap. imp. russk. techn. obschtsch., 1896, XXX, pt. 6–7.

A modification, perhaps of the interlocking theory, is that which suggests that the structure of the particles and their mode of aggregation may exert an important influence.

Mellor [1] suggests that a distribution of grain sizes which permits closest packing gives maximum plasticity.

Against this Schurecht [2] has argued that plasticity is greater with loosely cemented aggregates, finer-grained aggregates, and flocculated aggregates.

He further expresses the opinion that those clays which retain their plasticity after the finer particles are removed, have large compound particles, which break down easily on stirring, yielding a fresh supply of fine grains.

Ball theory.—Aaron suggested that the plasticity of clay was due to the presence of globular particles, but Zschokke has disputed this, on the ground that if the grains were of this form they would, when in closest contact (as when air-dried), touch at the fewest number of points,—a condition, therefore, not favorable to the great cohesion which exists between the grains of highly plastic clays.[3]

Colloid theory.—The theory that the plasticity of clay is due largely or entirely to colloidal matter is one which in one form or another is widely accepted at the present time, and has been the subject of numerous articles in the technical press.

The presence of colloids in clay was suggested at a comparatively early date, for Way [4] in 1850, while endeavoring to explain the high absorptive powers of clay for water, found that this property was destroyed by exposure to high heat, and considered that it was due to some peculiar form or modification of aluminum silicate which formed the clayey or impalpable portion of the soil. In searching for evidence he was able to prepare an artificial hydrated sodium aluminum silicate which possessed high absorptive properties.

Schlossing in 1874 [5] applied the theory of colloid suspension to explain the action of clay suspensions when electrolytes are added to them. After allowing the suspensions to stand for twenty-seven days, the solution with the remaining suspended material was evaporated to dryness, and the sediment which was horny he termed colloidal material.

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[1] Trans. Cer. Soc., XXI, p. 91, 1921–22.

[2] Bull. Amer. Cer. Soc., 153, 1922.

[3] See also Wolf, Tonindus.-Zeit., XXX, p. 41, 1906, and Rohland, Sprechsaal, XXXIX, p. 758, 1906.

[4] Royal Agric. Soc. Jour., XI, 1850. Quoted by Cushman, Trans. Amer. Ceram. Soc., VI, p. 7, 1904.

[5] Comp. rend., LXXIX, pp. 376 and 473, 1874; see also Durham, W., Chem. News, XXX, p. 57, 1874.

At a somewhat later date (1893), Van Bemmelen[1] announced, as the result of his investigations on the inorganic colloids or hydrogels, that "nearly all metallic oxides and many salts have the power of entering into that peculiar hydrated, non-crystalline condition which Graham[2] in 1861 denominated colloid or glue-like. The special hydrogel which Van Bemmelen studied most minutely was that of silicic acid, although his researches included the oxides of copper, tin, iron, aluminum, etc. As a result of these extensive investigations the author cited adopts the suggestion of Nageli of the micellian structure of colloids, that is to say, that these curious substances consist of heterogeneous molecular complexes which possess a submicroscopical, web-like, porous formation, one of the distinguishing characteristics of which is the peculiar relation to and dependency on water which they exhibit. The water-content of these hydrogels varies continually with the temperature and the vapor pressure of the atmosphere in which they find themselves. Dried at high temperatures up to a certain critical point, they will lose nearly all their water, only to take it back again eagerly when allowed to cool in free air or in moist atmospheres. This dehydration and rehydration can be repeated indefinitely, unless the temperature of drying is carried too high, when the faculty is gradually lost and finally destroyed.

"The water thus absorbed is denominated 'micellian' water, and differs from hygroscopic water in the ordinary sense of the word. It is absorbed into the particles of a powder of an inorganic hydrogel without changing the physical appearance when under the microscope, while hydroscopic water is usually absorbed on the particles producing a distinct appearance of wetness."

Some clays undoubtedly contain large amounts of colloids, but in others, as in many common clays, it is claimed that there is but a small proportion of ingredients which are capable of assuming the colloid state by the action of the water alone.[3]

Schlossing[4] states that in all kaolins there are finely crystalline substances and colloidal ones, which latter he separated by treatment with ammoniacal water, and found them to be singly refracting, globular aggregates, but Kasai,[1] on the other hand, disputed the existence of colloidal matter, for he finds that the apparently colloidal bodies of Zettliz kaolin are doubly refracting.

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[1] Zeitschr. anorg. Chem., V, p. 466; XIII, p. 233; XVIII, p. 14; XX, p. 185; XXII, p. 313. Quoted by Cushman, Jour. Amer. Chem. Soc., XXV, No. 5, May, 1903.

[2] Phil. Trans. (1861), p. 183. Quoted by Cushman, l. c.

[3] Ia. Geol. Surv., XIV, p. 90, 1904.

[4] Comp. rend. 1874, LXXIX, pp. 376 and 473.

Rohland, who has written considerable on the plasticity of clay, published his first paper in 1902 [2] and no doubt was inspired by the work of Graham and Schlossing.

In this paper he states that when clay dries, the colloidal matter shrinks and becomes hard and horny, its gelatinous properties being lost. In its condition of normal plasticity therefore the colloidal matter of the clay would be in the form of a gel. On addition of water it passes into a sol, and the addition of an excess of water gives us a clay slip.

Lucas [3] in commenting on Rohland's observation calls attention to the fact that Zettlitz kaolin must have some colloidal matter because it flows freely through a die, and regards as significant the fact that a non-plastic crystalline powder will, under pressure, allow the water to be squeezed out, and will only form a plastic mass when tragacanth is mixed with it.

The theory of Olchewsky that plasticity was due to the spongy porous nature of the smallest particles, which by reason of pressure arrange themselves into a sort of felt, may be regarded as admitting the presence of colloidal matter, but of more definite character are the statements of Arons[4] and Bischof, who suggest that plasticity was no doubt due to some special form of hydrated aluminum silicate, while Seger [5] remarks further that there is probably some effective molecular arrangement, which was already fixed in the structure of the parent rock.

In studying the clays of Maryland the author [6] noted the presence of what he assumed were colloidal bodies in the highly plastic clays, and the subject has been followed up in greater detail by Cushman,[7] who believes that plasticity is due to a " colloid condition of the fine particles, or of some proportion of the particles which go to make up the clay mass. These amorphous inorganic particles possess a submicroscopic structure. They absorb water eagerly, and gradually assume the coherent condition which causes in the wet mass the quality we call plasticity."

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[1] Die Wasserhaltigen Aluminum Silikate. Diss. München, 1896.

[2] Int. Mitt. für Bodenkunde, III, p. 492, 1913; also Zeit. f. angew. Chem. XXXI, Pt. I, p. 158, 1902.

[3] Geol. Centralb. f. Min., Geol. u. Pal., No. 2, p. 33, 1906.

[4] Dammer, Chem. Tech., I; Notizbl, IX, p. 167.

[5] Tonindustrie-Zeitung, p. 37, 1877.

[6] Md. Geol. Surv., Vol. IV, p. 251.

[7] Jour. Amer. Chem. Soc., XXX, p. 5.

In order to prove the existence of colloids in clays, Cushman[1] prepared some silicic acid. This jelly dries rapidly to a powder, which is hydrated and loses or gains water with changes in the moisture content of the atmosphere in which it stands, but if heated above 1000° C. it loses its absorptive power. Hydrated colloid alumina was also prepared artificially.

On mixing the former with clay[2] it was found that the silicic acid increased the binding power and shrinkage but not the plasticity; while the alumina increased the plasticity but not the shrinkage or binding power.

A mixture of the two, prepared by adding sodium silicate (water glass) to the solution of alum,[3] showed that its addition to a clay increased both its binding power and plasticity.

Ries[4] found that the addition of 1 per cent gallotannic acid to a clay appeared not only to increase its plasticity but also its binding power.

Grout[5] by using a dilute solution of agar-agar for tempering two clays found that 0.08 per cent increased their plasticity approximately 60 and 36 per cent, respectively.

He dried the same mass, mixed it with water, filtered off the latter, and tested the clear filtrate for soluble salts, but got no jelly, which was probably due to the fact, overlooked by him, that the clay adsorbs the colloidal material. (See Adsorption.)

Alumina cream was then tried instead of agar-agar, and it was found that it took 3 per cent of the former to raise the plasticity as much as 0.08 per cent of the latter; furthermore, after air-drying, powdering and remixing, the plasticity of the mass dropped to its original figure. Grout consequently argues that since plastic clays are not injured by air-drying, it is evident that "such colloids as alumina cream do not explain plasticity, and that some colloid is required which will soften in water after air-drying, a type which is extremely rare in the inorganic kingdom." He says further: "The suggestion of Cushman, that a hydrated silicate of alumina could be precipitated so as to give the desired properties, has been carefully tried, but all resulted exactly as alumina cream."

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[1] Trans. Amer. Cer. Soc., VI, p. 7, 1904.

[2] The percentage added is not given.

[3] The suggested formula of this mixture is $XAl_2O_3,YSiO_2,ZH_2O$.

[4] Trans. Amer. Cer. Soc., VI, p. 44, 1904.

[5] W. Va. Geol. Surv., III, 1906.

Grout, moreover, questions the value of detecting colloids by staining with methylene blue, since he finds that most clays contain from 1 to 5 per cent of grains which will take a stain from methylene blue, gentian violet, eosine, or fuchsine. Both fresh and dried silicic-acid jelly he states take the stain, but the latter acts like quartz in decreasing the plasticity. Weathering, he further claims, does not increase the number of grains capable of taking the stain.

It would appear from what has been said that most clays contain (1) both non-plastic bodies or grains, of either crystalline or amorphous character, and (2) colloids, which appear to at least influence the plasticity.

If the colloids are the main cause of plasticity, this fact is not proven definitely either by showing their presence in the clay or by demonstrating that their addition to an already plastic clay increases its plasticity.

On the contrary, it would seem necessary to add them to some fine-grained mineral aggregate of exceedingly low plastic qualities, and by this addition be able to change it into a thoroughly plastic mass. A mass of colloidal material by itself does not show the solidity and cohesiveness which a strongly plastic clay does. It is as if it lacked some strengthening internal structure, such as a mass of mineral grains might supply.

To endeavor to state the colloidal idea of plasticity in general terms we may say that it assumes that the clay grains are surrounded by a film of colloidal material, and that these grains are of non-plastic character. This colloidal material, which may vary in its composition is in a film of water, this mixture giving us a viscous fluid. This colloidal fluid acts as a cementing film which holds the mass together and gives the material properties which are intermediate between those of a solid and a liquid. That colloidal matter undoubtedly has some effect is shown by the fact that the addition of it has been found to increase the plasticity of some clays.

In most cases it seems as pointed out by several writers including Rohland and Davis that much of the colloidal matter in clay has probably been derived by the action of water on the mineral particles, which become surrounded by a colloidal film that is more or less intimately associated with them and difficult to separate.

For those who care to follow this subject farther the references given below may prove of interest.[1]

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[1] Ashley, H. E., The colloid matter in clay, Trans. Amer. Ceram. Soc., XI, p. 530, 1909; Atterberg, A., The plasticity of clay, Internat. Mitt. Bodenkunde, I, 4, 1910; Atterberg, A., The plasticity and coherence of clays and loams, Chem. Ztg.,

In trying to explain the mechanism of plasticity, G. A. Bole[1] advances the theory that the film of colloidal matter surrounding the clay grains is of opposite polarity to them. The addition of electrolytes acting as a deflocculant causes the outer layer of the film to be attracted to ions of same polarity as the clay particle, thus reducing the effective diameter and increasing the polarity of the plasticity inducing particles. Particles which were held by surface forces of " particles in contact " are no longer in contact and are actually repelling each other due to like and increased polarity. "A flocculating ion drives action in the opposite direction causing an increase in the depth of the colloidal film, thereby increasing the surface in actual contact and decreasing the repulsive force of plasticity-inducing particles. Transport numbers as well as polarity are governing factors in ions of electrolytes."

Action of water on silicates.—Rohland[2] has pointed out that the plasticity of clay " depends on the amount of hydrolysis which the material has undergone." Kaolin which is scarcely hydrolyzed has low

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XXXIV, p. 369, 1910; Bingham, E. C., Plasticity, Jour. Phys. Chem., XXIX, p. 1201, 1925; Bleininger, A. V., The viscosity of clay slips, Trans. Amer. Ceram. Soc., X, p. 389, 1908; Bleininger, A. V., The effect of electrolytes on clay in the plastic state, 8th Internat. Cong., App. Chem.; Bleininger, A. V., The properties of clay, Colloid Symposium, II, p. 80, 1925; Bleininger, A. V., and Brown, G. H., Note on the viscosity of clay slips, Trans. Amer. Ceram. Soc., XI, p. 596, 1909; Bleininger, A. V., and Clark, H. H., Note on the viscosity of clay slips determined by the clark apparatus, Trans. Amer. Ceram. Soc., XII, p. 383, 1910; Bleininger, A. V., and Fulton, C. E., The Effect of acids and alkalis on clay in the plastic state, Trans. Amer. Ceram. Soc., XIV, p. 827, 1912; Bleininger, A. V., and Ross, D. W., The flow of clay under pressure, Trans. Amer. Ceram. Soc., XVI, p. 392, 1914; Durham, W., Chem. News, XXX, p. 57, 1874; Ehrenberg, P., Plasticity, especially of barium sulphate, Zeitschr. angew. Chem., XXIV, p. 1957, 1911; Hall, F. P., Effect of hydrogen-ion concentration on clay suspensions, Jour. Amer. Ceram. Soc., VI, p. 989, 1923; Hall, F. P., Methods of Measuring the plasticity of clays, U. S. Bur. Stand., Tech. Pap. 234; Krupsay, Zur frage der bildsamkeit der tone, Tonind-Zeit, XXXII, p. 1289, 1908; Leppla, G., Die bildsamkeit der tone, Baumaterialienkunde, IX, p. 124, 1904; Mellor, J. W., Trans. Ceram. Soc. (Eng.), XXI, p. 91, 1921; Ries, H., N. J. Geol. Surv., VI, p. 83, 1904; Rohland, P., Plasticity of clay, Zeit. anorg. Chem., XXXI, p. 158, 1902; Rohland, P., The means of altering the amount of plasticity of clays, Sprechsaal, XXXIX, p. 1371, 1906; Rohland, P., The causes of plasticity and the allied properties of clays and kaolin, Silicat-Zeit., II, p. 30, 1911; Rosenow, M., The plasticity of clay, Tonind.-Zeit., XXXV, p. 1261, 1911; Stewart, J., The plasticity of clay, Jour. Ind. Eng. Chem., V, p. 421, 1913, and 8th Internat. Cong. App. Chem., XV, p. 265; Van Bemmelen, Archiv. Neerland Sci. Exactes et Nat., Ser. III*a*, Vol. I, pp. 1–14, 1912; Van der Bellen, Chem. Zeit., XXVII, No. 36, p. 433, 1903; Wilson, R. E., and Hall, F. P., The Measurement of the Plasticity of clay slips, Jour. Ind. Eng. Chem., XIV, p. 1120, 1920.

[1] Jour. Amer. Ceram. Soc., V, p. 469, 1922.

[2] Sprechsaal, XLI, p. 447, 1908.

plasticity, while very plastic ball-clays are highly hydrolyzed. In harmony with this are the conclusions of H. Gedroiz [1] who asserted that aluminum hydroxide, ferric hydroxide, silicic acid, and kaolinite, are, at the moment of their formation by weathering, hydrosols, which remain as such or are coagulated, depending on the composition of the soil solution.

This would also explain why the outlines of the solid particles of wet ground feldspar could be more readily stained with dyes than before the water treatment.[2]

Davis experiments.[3]—Davis working on very plastic clays selected a series of four which were suspended in distilled water and allowed to stand. It was found that the particles did not settle with equal rapidity, the difference in the suspensions suggesting a possible difference in the nature of the colloid present. It was also noticed that of the suspensions remaining at the end of twenty days both contained colloidal organic matter and colloidal silica, but that the former was most abundant in the sample of which a greater quantity of suspension remained.

As Davis points out the organic colloid may have the effect, as an emulsoid of increasing the viscosity of the suspension, or it may act as a protective colloid coating.

It is probable that two of the clays contained some colloidal iron oxide gel, since they burned red.

Organic colloid gels according to Grout [4] have a greater effect on plasticity than inorganic colloid gels.

Addition of organic matter.—Davis found that mixing 2 lbs. of Delaware washed kaolin with 1 ounce of peat, grinding for ten hours in a ball mill, then drying out the slip and mixing the mass with water, the plasticity had increased, the shrinkage increased from 4 to 8 per cent, but there was little increase in the tensile strength.

Other experiments have been recorded by Zimmer,[5] Grimsley and Grout,[6] and Ashley.[7]

Organic colloids are relatively prominent in some clays, especially some very plastic ones and since they tend to raise the viscosity of the water film, they increase the plasticity.

If this is correct then the treatment of such clays by organic solvents should reduce the plasticity.

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[1] J. Exp. Landw., pp. 272–293, 1908.

[2] Mellor, Trans. Ceram. Soc., (Eng.) V, p. 72.

[3] Davis, Trans. Amer. Inst. Min. Engrs., LI, p. 445, 1915.

[4] W. Va. Geol. Surv., III, p. 80, 1905.

[5] Trans. Amer. Ceram. Soc., III, p. 36, 1901.

[6] W. Va. Geol. Surv., III, p. 48, 1905.

[7] U. S. Bur. Standards, Tech. Pap. 23, p. 82, 1911.

Nolte,[1] after treating a heavy Silesian clay with ethyl ether and acetone, did not find the plasticity diminished. Hamor and Gill,[2] on the other hand, found that certain American clays when treated with organic solvents such as benzol, alcohol and carbon tetrachloride, show a decreased plasticity, but it was not the same for different solvents.

Pfefferkorn [3] claims that the extraction of organic matter does not alter the plasticity.

Soluble salts.—These also appear to have an effect on the plasticity of a clay. Seger,[4] and Purdy and Moore [5] have gone so far as to consider it a reasonable assumption that these adsorbed salts give the clay its plasticity.

Grout and Poppe [6] note that " the essential peculiarity of a plastic clay is the fact that the water used in wetting it is somehow rendered viscous. In explanation we have two well-known phenomena, molecular attraction and the action of colloids. Both are certainly present. Both are necessarily active." They believe that the former may be quantitatively sufficient, and that the latter would be quantitatively insufficient.

Considerable opposition to the colloidal theory has been expressed by Purdy, although he admits that the presence of colloidal matter may be a contributing cause.

He among other things disputes the idea of colloidal coatings forming around mineral grains [7] as proposed by Davis and others, in fact he claims that clays do not form typical colloidal solutions, and that only a small portion of the clay roughly approximates such. He even asserts that bentonite, which according to him is the nearest approach to a true colloidal solution,[8] has adhesiveness but lacks cohesiveness. This last statement may also be open to dispute, since bentonite is used as a bonding medium in certain foundry sands.

Purdy also holds that " any or all portions of any clay, the coarse grains of which are high in clay substance (as determined by chemical analysis) will be about as plastic and have about as high strength as the clay bond had before removal of the portions that approach true colloidal solutions."

Some very significant experiments bearing on Purdy's contention that removal of fine material does not reduce the plasticity have been reported on by Moore, Fry and Middleton.[1]

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[1] Biedermann's Zentr., XVII, p. 108, 1918.

[2] Jour. Amer. Ceram. Soc., II, p. 594, 1919.

[3] Sprechsaal, LVIII, p. 183, 1925, and LVII, p. 297, 1924.

[4] Collected Writings.

[5] Trans. Amer. Ceram. Soc., IX, p. 222, 1907.

[6] Trans. Amer. Ceram. Soc., XIV, p. 71, 1912.

[7] Bull. Amer. Ceram. Soc., I, p. 147, 1922.

[8] This may not be agreed to by all investigators.

These authors in working up large quantities of soil for the study of the constitution of the soil solution, used a large centrifuge which had a force up to 18,000 gravity to assist in clarifying the solution. There remained in the latter an opalescence which could be removed by the Pasteur-Chamberland filter. This opalescent material accumulated on the filter as a slimy sticky mass, and was called "*ultra clay*."

They state that chemically it is a silicate of alumina with some iron and small but varying amounts of calcium, magnesium, sodium, and potassium, but whether these were chemically combined or physically adsorbed was not known.

This ultra clay they state when suspended in water showed the form and properties of a true colloid, and under the ultra microscope appeared as droplets of an amber yellow color immiscible with water. If the suspensions are thick the droplets coalesce. They also coalesce on the addition of electrolytes.

When clays are freed of this ultra clay by elutriation and subsidence, the clay loses much of its plasticity. This ultra clay when moist is exceedingly plastic.

The following experiments were made to determine the adhesive power of the ultra clay, and they show that it has a greater binding power than Portland cement:

Experiment series 1. A standard grade of sand was mixed with 10 per cent of the substances named below. These mixtures were molded into "briquettes," 25 mm. high and 25 mm. diameter, with 18 per cent moisture. They were molded under a pressure of 1800 lbs. per square inch and dried at 100° C.

The crushing strength in kilos of the different 10 per cent binders was as follows: Portland cement, 19.16; Cecil ultra clay, 122.52; Susquehanna ultra clay, 96.39; commercial kaolin, 0.00.

Experiment series 2. In these quartz flour was used instead of sand. The results were: Portland cement, 112.30; Cecil ultra clay, 304.64; Susquehanna ultra clay, 206.82; commercial kaolin, not tried.

With 2 per cent. of the binder the results in this last series gave: Portland cement, 72.89; Cecil ultra clay, 65.54; Susquehanna ultra clay, 69.70; commercial kaolin, 17.96.

The ultra clay has a very high absorbent power for certain mineral matters, certain organic matters, and certain gases.

The authors consider that the ultra clay is the cause of the plasticity.

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[1] Jour. Ind. Eng. Chem., XIII, p. 527, 1921.

Molecular-attraction theories.—Several writers, to be referred to below, have inclined to the theory that the plasticity of clay was due to molecular attraction between the clay particles themselves or between the clay grains and water surrounding them.

Ladd,[1] as a result of his work on the Georgia clays, advocates the theory that the mutual attraction between water and clay particles, and surface tension of the water-films, may exert an important influence in determining plasticity.

The affinity of the clay particles for water will, however, vary with their chemical nature; [2] and particles of the same material have a varying affinity, under different conditions not now well understood. Moreover, salts and organic matter, in solution, modify the value of the surface tension of the liquid, the former generally increasing, the latter decreasing. This latter seems an important point for all clays containing a variable quantity of soluble matter.

The importance of molecular attraction between the clay substance and water was looked on by Zschokke [3] as an important cause of plasticity, he having pointed out that since clay particles are plastic bodies, they have greater attraction for water than non-plastic grains such as sand, and that therefore the grains will be surrounded by a thicker film of water than sand-grains would be. The addition of an excess of water separates the clay-grains so far that they are no longer able to attract each other, and the mass loses much of its cohesiveness. Moreover it is thought that the absorption of the water into the pores of the clay is accompanied by a superficial alteration of the clay particles, giving them a gelatinous coating, which permits them to change their form and at the same time keep in close contact; a point which is rather corroborated by the experiments of Cushman [4] and Mellor.[5] He finally suggests that plasticity must be dependent on (1) the size of the smallest particles; (2) the form and character of the surface; and (3) other peculiar properties possibly of a molecular character.

Grout,[6] reasoning along somewhat similar lines, believes that the chief cause of plasticity is the molecular attraction depending on the chemical constitution of molecules, but that it may be improved by the addition to the clay of colloids such as tannin, etc., or such solutions as ammonia, alum, etc.

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[1] Ga. Geol. Surv., Bull. 6*a*, p. 29, 1898.

[2] Whitney, U. S. Dept. of Agric., Bull. 4, 1892; Briggs, ibid., Bull. 10, 1897.

[3] l. c.

[4] Bull. U. S. Dept. Agric., 92, 1905.

[5] Trans. Ceram. Soc. (Eng.), V, Pt. I, p. 72, 1905–6.

[6] W. Va. Geol. Surv., III, p. 54, 1906; see also MacMichael, Trans. Amer. Ceram. Soc., XVII, p. 616, 1915; Chatley, H., Trans. Ceram. Soc. (Eng.), IX, p. 1–2, 1919–20.

General comments.—While several of these theories—plate structure, texture, colloids, and molecular attraction—have much to commend, still there seem to be serious objections in many cases to their being the *sole cause* of plasticity. Indeed the examination of any extensive series of clays hardly seems to bear out the theory that any one of the causes suggested is the sole one, but rather that plasticity may be dependent on a combination of them.

The writer is to some extent in sympathy with Purdy[1] when he expresses the belief that plasticity is the result of such properties as adsorption, solution, molecular attraction and high surface tension. He might have obtained more adherents to his views if he had also admitted the existence of colloidal films around the particles. And yet clays may be plastic enough to mold, even though they apparently contain a very small colloid content.[2]

To quote Purdy he adds, that the properties which he enumerates "cause the particle when wetted to hold a water-saturated film. For the mass to exhibit plasticity, the particles must not be separated one from the other beyond the range of molecular attraction, one with the other, which range is sufficient to permit each to retain its maximum water envelope. Experiments have shown that the volume of water required to render the clay plastic is equal to the volume of water required to fill the pores plus the water required to give each and all particles (or bundles of particles) its maximum water film. This salt solution is the "slippery medium" and when the mass is dried these salt coatings are the cementing agents, and when subjected to heat treatment they are the sintering media." This last point will probably not be accepted by all.

Effect of bacteria.—Aging a clay mixture, that is, allowing it to lie in cellars for six months or a year, appears to improve its plasticity, and it has been suggested that this is due to bacterial action. Bacteria are not uncommon in clay, and the prevalent one, according to Stover,[3] is believed to be bacillus sulphureus, whose development is facilitated by a temperature of 37° to 38° C.

Seger, although not referring to bacteria, stated that in the aging of a clay an acid was gradually developed by organic decomposition, which destroyed the alkalinity of the mass and was supposed to be responsible for the improvement in plasticity.

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[1] Trans. Amer. Ceram. Soc., XI, p. 588, 1909, and ibid., Bull. I, p. 150, 1922.

[2] Ries, H., Amer. Jour. Sci., (4) XLIV, p. 316, 1917.

[3] Trans. Amer. Ceram. Soc., IV, p. 185, 1902.

Spurrier has also observed that the plasticity of clay appears to increase with the growth of algae in it, and the presence of a hydrogel of alumina caused by a biochemical reaction.[1] The same author pointed out that the evacuation of air from the clay also caused increased plasticity.

Since bacteria are known to exist in clays, they may add organic colloids (protoplasm) to it, and thereby increase its plasticity.[2]

Weathering clay.—It is a well-known fact that weathering a clay often increases its plasticity, but this might be due to several causes, such as mechanical disintegration of the mass by frost, water soaking, the oxidation of organic matter, or to the production of colloids by hydrolysis or bacterial action.

Grinding may sometimes improve the plasticity as much as weathering.

Rohland states that it may be increased: (1) By contact with spring or river water; (2) decrease in temperature; and (3) addition of colloids.[3]

Water of plasticity.—It has been found that different clays require different amounts of water to develop their maximum plasticity as the following list taken from published data will show:

WATER OF PLASTICITY OF DIFFERENT KINDS OF CLAY.

Crude kaolin	36.69 – 44.78
Washed kaolin	44.48 – 47.50
White sedimentary kaolin	28.60 – 56.25
Ball clays	25.00 – 53.30
Crucible clays	26.84 – 50.85
Refractory bond clays	32.50 – 37.90
Glass-pot clays	19.64 – 36.50
Plastic fire clays	12.90 – 37.40
Flint fire clays	8.89 – 19.04
Sagger clays	18.40 – 28.56
Stoneware clays	19.16 – 34.80
Face brick clays	14.85 – 37.50
Sewer pipe clays	11.60 – 36.20
Paving brick clays	11.80 – 19.60
Brick clays	13.20 – 40.70

The amount of water required for developing the maximum plasticity in a clay may be affected by soluble salts, organic matter and acids.

Thus the addition of alkali usually tends to decrease the amount needed, although Rohland[1] found that it increased the amount. Schurecht notes that acids in small quantity increase the amount of water required, while larger percentages decrease it, while Bleininger and Fulton[2] state that acids increased the water of plasticity but decreased the drying shrinkage.

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[1] Spurrier, H., Jour. Amer. Ceram. Soc., IX, p. 535, 1926.

[2] Grimsley, G. R., and Grout, F. F.,W. Va. Geol. Surv., III, p. 47, 1906.

[3] Sprechsaal, XLII, p. 1371.

According to Mellor,[3] and Bourry,[4] the water of plasticity decreases with an increase in the pressure used for molding.

Effect of electrolytes.[5]—The effect of electrolytes on clay suspensions as well as on plastic clay is of much importance, since they probably affect the plasticity as well as influencing flocculation and deflocculation.

Acids, acid salts, lime sulphate, common salt, and most salts of the metals cause flocculation.

Ammonia, hydroxides and carbonates of the alkalies, as well as their borates, and silicates bring about deflocculation or peptization.

Salts which dissociate into acid and basic ions may cause either flocculation or deflocculation.

Alkalies for example by increasing the dispersion of the clay particles reduce the viscosity of the suspension. This is explained by the negatively charged OH ions, which repel similarly charged particles electrostatically, and therefore increase the dispersion of the system or cause deflocculation. A definite concentration of OH ions gives the maximum effect, and should the concentration go beyond this, the effect is reversed, and we get increased viscosity, or flocculation, but with a further addition of alkali the viscosity is again reduced.

The presence of soluble salts in a clay may interfere with its deflocculation, or in making a slip with it, in fact Searle has stated that the presence of .002 per cent of calcium sulphate may act as such a preventive.

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[1] Die Tone, p. 85.

[2] Trans. Amer. Ceram. Soc., XIV, p. 827, 1912.

[3] Trans. Ceram. Soc. (Eng.), XXI, p. 25, 1921-22.

[4] Treatise on Ceramic Industries.

[5] Bleininger, A. V., and Fulton, C. E., The effect of acids and alkalies upon clay in the plastic state, Trans. Amer. Ceram. Soc., XIV, p. 827, 1912; Bleininger, A. V., Note on the electrical separation of clay, Trans. Amer. Ceram. Soc., XV, p. 338, 1913; Brown, H. G., and Howat, W. L., Use of deflocculating agents in the washing of clays, Trans. Amer. Ceram. Soc., XVII, p. 81, 1915; Comber, N. M., The mechanism of flocculation in soils, Trans. Far. Soc., XVII, Pt. 2, p. 349, 1922; Kerr, C. H., and Fulton, C. E., The effects of some electrolytes on typical clays, Trans. Amer. Ceram. Soc., XV, p. 184, 1913; Smith, O. M., The coagulation of clay suspensions, Jour. Amer. Chem. Soc., XLII, p. 460, 1920; Schurecht, H. G., The use of electrolytes in the purification and preparation of clays, U. S. Bur. Mines, Tech. Pap. 281, 1922.

Davis (l. c.) noted that one clay containing soluble salts which he tested settled very rapidly from suspension.

Several explanations have been advanced however to explain the cause of flocculation and deflocculation.

One is that of the electrical charges mentioned above.

Another is that if in a water-clay system there is a stronger attraction between solid-liquid molecules than between the molecules of the liquid, the water-films around the clay particles enlarge, and the grains are kept apart: If the reverse is true, the particles approach each other more closely and flocculation ensues.

Purdy's theory[1] is that flocculation and deflocculation are due to the difference in the surface tension of the water, which is in excess of that required to develop plasticity, and the surface tension of the water film.

Ashley[2] held that the deflocculation and flocculation are the result of chemical reactions. He states that the fine crystalline grains are enveloped by a colloid coating which enters into "chemical reactions remarkably similar to those of the fats and soaps, in that the alkali sols of clay colloids are soluble and the acid gels of the clay are insoluble. Both soaps and clay sols may be salted out of solution by dissolving in the solution chemical salts that have more affinity for water than have the soaps or gels salted out."

Attempts to separate colloids from clay have not always yielded large results.

Schlossing[3] succeeded in removing from a kaolin 1.47 per cent of very fine material, which remained in suspension twenty-seven days.

Mellor[4] was able to remove 0.05 per cent of glue-like material from a Devonshire ball-clay, but only 0.005 per cent from a china-clay, while Vasel claimed that the Meissen, Saxony, kaolin contained at least 3 per cent colloid clay, whose composition corresponded to $Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$.[5]

It seems probable that some very plastic clays contain a high percentage of colloidal matter. Some experiments by Davis,[6] showed that at the end of twenty days considerable material remained in suspension. In two of these particles were not visible with a magnification of 600 diameters, but in the third they measured 0.002 mm. in diameter.

Robinson and Holmes, in working on clay soils, were able in some cases to extract as high as 38 per cent of colloidal matter, whose particles did not exceed 0.3 micron in diameter.[1]

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[1] Bull. Amer. Ceram. Soc., I, 1922.

[2] U. S. Geol. Surv., Bull. 338.

[3] Comptes rend., LXXIX, p. 376–80, 437, 1874.

[4] Trans. Ceram Soc. (Eng.), VI, p. 989, and XXI, p. 91.

[5] Kolloid-Zeit., XXXIII, p. 178, 1923.

[6] Trans. Amer. Inst. Min. Engrs., LI, p. 465, 1915.

The principle of deflocculation is made use of in the washing of clays and also in casting pottery. In the latter the adding of an alkali reagent like Na_2CO_3 or Na_2SiO_3 greatly reduces the quantity of water required to maintain the body in a liquid condition.

As pointed out by Mellor, clay slip with 0.3 per cent of a mixture of sodium carbonate and silicate, contains less water than a stiff mass of clay without alkali. If a little acid is added to neutralize the alkali, the mixture becomes solid. If more alkali is added the material becomes fluid again.

Source of colloids in clays.—Many writers make reference to the existence of colloids in clays, without giving much attention to their derivation, especially of the inorganic ones, and it would seem that a consideration of this factor would serve well to explain why it is that certain clays are often much more plastic than others, especially if we consider that colloids are undoubtedly an important factor in plasticity.

The relation of colloidal material to the past history of the clay has been well emphasized by Davis.[2] As shown by him dry ground rock powders develop practically no plasticity and no colloidal matter. Such powders if ground in water for a long time, do develop some plasticity, which is due to the solvent action of the water on the mineral grains, resulting in a colloidal solution. The amount of gel matter in a deposit therefore depends on its past history, and the length of time that the material has been exposed to the action of water. As Davis concludes: " Clays are simply weathering products of rocks, in which the most soluble constituents have been removed, leaving behind some resistant secondary products with gelatinous coatings."

This incidentally brings out the additional fact that a complete and satisfactory explanation of the properties of clay cannot be worked out in the chemical laboratory alone, but must give some consideration to the geologic conditions surrounding its formation.

MEASUREMENT OF PLASTICITY

Clays vary widely in their plasticity ranging from those which are very lean or low in plasticity, to those which are very fat or of high plasticity.

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[1] U. S. Dept. Agric., Bull. 1311, p. 19, 1924; see also Bulls. 1122 and 1452. Fry, W. H., Microscopic estimation of colloids in soil separates, Jour. Agric. Research, XXIV, p. 879, 1923.

[2] Trans. Amer. Inst. Min. Engrs., LI, p. 451, 1915.

Many methods for measuring plasticity have been suggested, but objections have been urged against most of them, mainly on the ground that they are empirical, and also as claimed by some that they measure not plasticity, but some property closely allied to it.

Hall calls attention to the fact [1] that the heterogeneity of the system water-clay, makes it difficult to formulate mathematical equations that are satisfactory. The consistency of a water-clay mixture he claims is influenced by such factors as: (1) Past history of the clay, (2) type of clay, (3) amount of working the mixture has received, (4) time of contact of clay and water, (5) temperature of mixture, and (6) amount of water. Some of these factors are hard to control, and unless kept constant, a comparison of different tests becomes difficult.

The tests which have been suggested fall into two groups, those of the wet and those of the dry clay, the former being the more logical.

Tests of the wet clay.—A common and practical method consists in judging the plasticity by feel, grading it as poor, good, high, etc.

Bischof [2] suggested forcing the wet clay through a cylindrical die, and measuring the length of the pencil extruded before it broke of its own weight, and a similar method has been recommended by E. C. Stover,[3] but these are open to the objection that the clay should be worked into its most plastic condition before testing, and there is no means of determining accurately when this condition has been reached. Indeed this criticism applies to many of the methods suggested.

Langenbeck [4] advocated forcing a Vicat needle into the clay by the pressure of a known weight, and stated that the proper consistency was reached when the needle under a weight of 300 grams penetrates to a depth of 4 c.c. in five minutes.

A similar method was suggested by Grout,[5] who measured the strength by the weight required to force a Vicat needle of 7 sq. cm. cross section to a depth of 4 cm. in one-half minute, and also by G. E. Ladd.[6]

Another method by Ladd [7] consisted in having two small sheet-iron troughs with perforated bottoms, in the center of which are set test-tube brushes, so placed that the ends of the brushes touch when the ends of the troughs are in contact. The dry clay is sifted into the brushes and water absorbed from below until the point of saturation is reached.

[1] Jour. Amer. Ceram. Soc., V, p. 346, 1922.

[2] Die feuerfesten Thone, p. 84.

[3] Trans. Amer. Ceram. Soc., VII, p. 397, 1905.

[4] Chemistry of Pottery, p. 19.

[5] Jour. Amer. Chem. Soc., XXVII, p. 1037, 1905.

[6] Ga. Geol. Surv., Bull. 6*a*, p. 51, 1898.

[7] Ga. Geol. Surv., Bull. 6*a*, p. 52, 1898.

The pull required to tear the column of clay between the brushes is measured by placing weights on a scale-pan attached to one of the troughs until the two separate.

The criticism urged against this method is that it gives little information regarding the plasticity, but measures the strength of the clay through different degrees of saturation.[1]

A somewhat detailed investigation is that of Zschokke.[2] According to him, it is necessary, in testing the plasticity of a clay, to consider (1) its property of deformability; (2) its degree of cohesion; (3) its stickiness or adhesiveness.

The degree of deformability was first tested by molding the thoroughly worked clay into cylinders 60 mm. high and 30 mm. in diameter, and subjecting these to pressure applied at the ends until cracks appeared, but this was found to be unsatisfactory, as some lean sandy clays were deformed more than highly plastic ones.

A more satisfactory method consisted in placing these freshly molded cylinders in a specially designed machine and pulling them in two. The amount of expansion showed the degree of deformability, while the force required to pull the cylinder in two showed the tensile strength. The product of the two Zschokke terms the plasticity coefficient. It was found that higher figures were obtained by stretching the bar rapidly, or by a succession of short rapid strokes. The following figures illustrate these points.

Rupture Experiments

Number of sample	Slow pull			Jerky pull			Per cent H_2O reg.
	Tensile strength β kgm. per sq. cm.	Deformability λ in per cent	Plasticity coefficient $\beta\lambda$	Tensile strength β kgm. per sq. cm.	Deformability λ in per cent	Plasticity coefficient $\beta\lambda$	
269	0.63	70	44.1	1.73	127	220	29.8
250	0.48	28.6	13.7	1.52	97	147	22.9
631	0.42	18.4	7.7	0.96	91	87	26.0
901	0.36	17.4	6.3	0.93	82	76	21.8
705	0.27	33.4	9	0.86	94	81	20.8
507	0.25	20	5	0.96	90	86	20.8
702	0.20	8.6	1.7	0.76	73	55	23.9
636	0.08	5	0.4	0.20	5	1	21.8

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[1] Ia. Geol. Surv., Vol. XIV, p. 100, 1904.

[2] l. c.

Commenting on the results of his tests Zschokke states that in very plastic clays there appears to be a slight amount of elasticity, so that it is necessary to distinguish between elastic and permanent changes of form.

Grout in his work on West Virginia clays[1] arrived at conclusions somewhat similar to those of Zschokke. He considers that plasticity may be considered as involving two variable factors, viz., (1) amount of possible flow before rupture, and (2) resistance to flow or deformation. "Plasticity" he says, "increases in direct proposition to each of these factors, and is therefore equal to the product."

He measured the plasticity by carefully mixing and tempering the clay, and then forced it through a thin-walled metal cylinder $\frac{3}{4}$ inch in diameter. A plunger forced the clay through this die, and the bar of clay was cut into 2-inch lengths.

These small cylinders were placed vertically under a movable plate and pressure applied, the amount necessary to compress it $\frac{1}{2}$ cm. being taken as the measure of resistance to flow or deformation.

The cylinder was then further compressed until the appearance of cracks at about 45° to the vertical line, and this was considered the point of fracture. Vertical cracks, due to tension as the cylinder "expanded, were disregarded, and an irregular swelling of the cylinder under pressure was an indication that the mass was not uniform." The amount of flow was measured by the increase in area of the head of the cylinder.

The resistance to flow was found to be more satisfactorily measured by use of a Vicat needle; a needle of 7 sq. mm. ($\frac{1}{8}$ in.) was used, and weight determined which was necessary to cause the needle to sink 3 cm. in $\frac{1}{2}$ min.

Stringer and Emery method.—J. W. Mellor[2] in describing the method of Stringer and Emery points out that the plasticity of a clay varies with the proportion of water. As water is added the plasticity increases to a maximum, above which it is reduced. The clay then assumes another form and as the particles no longer cohere, it becomes sticky, and with still further addition of water forms a slip.

The plasticity of the clay is tested by molding it into spheres 2 cm. in diameter, which are deformed under pressure. The degree of compression which the clay suffers without cracking and the weight required to compress it, determine the plasticity.

It was noted that the greater the molding pressure applied to the clay, the smaller the proportion of water required to develop the maximum plasticity.[1]

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[1] W. Va. Geol. Surv., III, p. 40, 1906; also Jour. Amer. Chem. Soc., XXVII, p. 1037, 1905.

[2] Trans. Far. Soc., XVII, p. 355, 1921-22.

Emley plasticimeter.[2]—In this machine which was designed originally for testing lime, the property of deformation under pressure and also water-retaining power are measured. It has not been considered as very satisfactory for clay.

Dye-adsorption test.—This test, suggested by Ashley, is based on the assumption that the plasticity of a clay is inversely proportional to its grain size, and hence the plasticity must increase with the colloid content.

Ashley determined the latter by noting the loss of color of a dye solution when mixed with clay, and comparing it with another similar solution to which a standard clay had been added.

Since different colloids may show different adsorptive powers for different dyes, this method is not altogether a satisfactory one because the colloids present may not all respond to the dye used. Moreover, since adsorption is a surface tension phenomenon, particles larger than colloidal ones might also adsorb some.

Ashley[3] used a plasticity factor expressed by the formula $c\frac{b}{a}$ in which c = relative colloid content; b = air drying shrinkage; and a = Jackson-Purdy surface factor.

c is determined by the amount of malachite green adsorbed from a 0.3 per cent water solution of the dye, expressed in terms of the quantity adsorbed by the same weight of a standard plastic clay. Ashley claims that this method is only an approximate method of measuring plasticity.

Atterberg method.—Atterberg[4] divided what he called the range of plasticity into five stages as follows:

a. Upper limit of fluidity, at which the clay flows almost like water.

b. Lower limit of fluidity, at which two portions of the clay will not flow together if jarred.

c. Adhesion limit, at which the clay ceases to stick to other objects.

d. Rolling out limit, at which the clay can no longer be rolled into thin cylinders.

e. Cohesion limit at which the grains cease to cohere.

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[1] See also Rieke, R., and Sembach, E., Ber. deut. keram. Ges., VI, p. 111, 1925, and Jour. Soc. Glass. Tech. (Abstracts), IX, p. 317.

[2] U. S. Bur. Stand., Tech. Pap. 169, and Trans. Amer. Ceram. Soc., XIX, p. 523, 1917.

[3] U. S. Geol. Surv., Bull. 388.

[4] Intern. mitt. Bodenkunde, I, pp. 4–37; Tonind.-Zeit., XXXV, p. 1460.

The working range of clays is said to be between *c* and *d*, while the limits *b* and *d* separate as the plasticity increases.

Atterberg's plasticity figure is obtained by deducting the water required for *d* from that for *b*. To test the plasticity of a clay it is necessary to work it up with increasing amounts of water, and determine the critical limits.

In making the test 5 grams of clay powdered to 120 mesh are put into a small porcelain evaporating dish and water added to form a paste. The mass is then spread out in a layer 1 cm. thick, a triangular groove is cut through the paste, and the dish tapped sharply against the hand. Clay is then added until the mass is so stiff that it will barely flow together. The water content is then determined. To determine the rolling limit the clay in a stiff condition is rolled on paper to form threads. Clay is then added until the threads crumble, when another water determination is made. This gives the rolling limit.

Kinniston[1] claims that the Atterberg plasticity number is of little significance, and suggests that if the plasticity number were multiplied by a factor, such as the water of plasticity, it would represent a better plasticity index. Rieke[2] has also objected to it. There seems no doubt that the personal equation factor must exert an important influence.

MacMichael torsional viscometer.[3]—The primary object of this instrument is to determine the viscosity of clay slips, which may be regarded as plastic substances rather than liquids.

The viscosity of a liquid is determined by a torsional balance consisting of two concentric cylinders, one suspended by a fine wire, thus forming a torsional pendulum. The outer one rotates at a constant speed, while the inner one rotates until the torsional force of the suspending wire balances the viscous resistance, remaining fixed to permit a reading. Quoting from Hall: " In the case of viscous liquids, if the speed of rotation of the outer cylinder is plotted against the angular deflection of the inner cylinder, the result will be linear and pass through the origin. If a plastic substance is tested, the result will be linear at high speeds but the linear portion of the curve extended will not pass through the origin but will intersect the deflection axis at a definite point above the origin. Clay slips behave like plastic substances in this instrument."

Hall claims that the results are not reproducible on account of what may be called a " puddling effect" due to local agitation in the slip.

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[1] Trans. Amer. Ceram. Soc., XVI, p. 472, and Bur. Stand., Tech. Pap. 46, 1915.

[2] Sprechsaal, XLIV, p. 597, 1911.

[3] Hall, F. P., Jour. Amer. Ceram. Soc., V, p. 348, 1922.

Bingham plastometer.[1]—In this instrument developed by E. C. Bingham, the rate of flow (of the plastic substance) through a capillary tube and under a definite constant pressure head is determined.

The flow at several pressures is determined, and the volume discharged per second is plotted against the pressure producing the flow. Like the MacMichael viscometer the relation for true viscous liquids is linear and passes through the point of origin, but for plastic substances the linear portion of the curve extended does not pass through the origin because a certain definite pressure must be exceeded before the substance will flow at all.

The slope of the line shows the mobility of the clay, and the intercept on the pressure axis shows the initial friction.

The factors of mobility and yield value, define roughly the plasticity of the substance.[2]

Wilson and Hall [3] note that the amount of water required to give constant mobility varies widely, and does not appear to bear any definite relationship to the usual classifications of more or less plastic clays, but that it probably does parallel fairly well the shrinkage in drying.

Small amounts of acid or alkali appear to have little effect on the mobility of a clay slip, but strongly affect its yield value. Hence the hydrogen-ion content of the water used in making clay slips should be carefully controlled.

A modification of the Bingham plastometer has been used by Wilson and Hall [4] in which a capillary tube, 5.02 cm. long and 1.3624 mm. diameter, was used.

The tables in Figs. 48 and 49, show respectively the effect of water content on the flow of a Tennessee ball-clay slip, and the flow of various clays with a constant water content.

Figure 50, taken from the same paper, is interesting in showing the behavior of a series of clays mixed with the proper amount of water to give them the same mobility. Leaving out the bentonite it is observed that the order in which the clays arrange themselves with respect to their yield value, corresponds pretty well with their relative plasticity as usually held.

To determine the relative plasticity of two clays, a slip of one clay

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[1] Proc. Amer. Soc., Test. Mat., XIX, II, 1919, and XX, II, 1920; Jour. Amer. Chem. Soc., V, p. 350, 1922.

[2] See also U. S. Bur. Stand., Sci. Pap. 278, 1916; Jour. Wash. Acad. Sci., VI, p. 177, 1916.

[3] Jour. Amer. Ceram. Soc., V, p. 916, 1922; also Jour. Ind. and Eng. Chem., XIV, p. 1120, 1922.

[4] Jour. Amer. Ceram. Soc., V, p. 916, 1922.

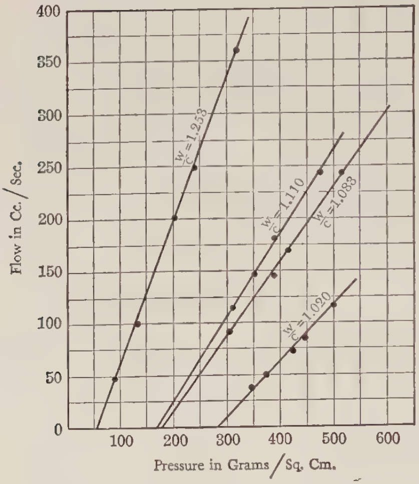

FIG. 48.

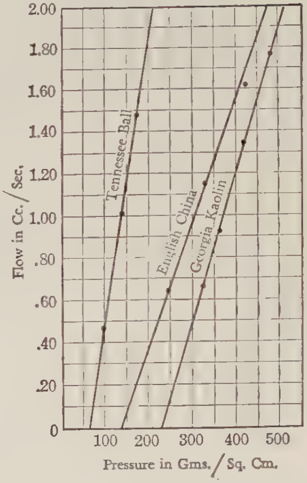

FIG. 49.

FIG. 48.—Effect of water content on flow of Tennessee ball clay slip. (Wilson and Hall, Jour. Amer. Ceram. Soc., V, 1922.

FIG. 49.—Flow of various clays with constant water content. $\frac{W}{C} = 1.253$. (Wilson and Hall, Jour. Amer. Ceram. Soc., V, 1922.)

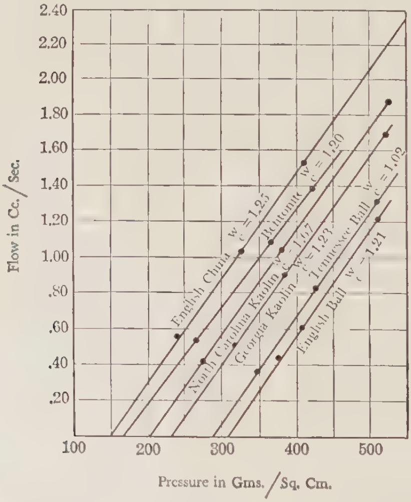

FIG. 50.—Comparison of yield value and water content at constant mobility. (Wilson and Hall, Jour. Amer. Ceram. Soc., V, 1922.)

is made up and its mobility and yield value determined. Then a second clay slip is made up and its water content varied until its mobility equals that of the first, using the same capillary tube.

With the mobility constant, the plasticity will vary directly as the yield value.

Miscellaneous methods.—Some have suggested using the amount of water of plasticity; the per cent drying shrinkage in terms of the original clay volume; or the ratio of the volume of pore water to the volume of shrinkage water, as a means of expressing the plasticity, but none of these are satisfactory.

Bole,[1] in pointing out the unsatisfactory character of the different methods suggested for determining plasticity, selected five different clays, and asked as many observers to judge their plasticity by touch. The clays were all made up to maximum plasticity before the test. Each observer made three determinations by the touch or feel method, the first two blindfolded and the third unrestricted. The identity of the samples was unknown to the observer at the time of testing. The results are given below:

ORDER OF PLASTICITY OF CLAYS AS JUDGED BY OBSERVERS USING TOUCH METHOD AND BASIS FOR JUDGMENT

Clay	Tenn. ball			Weathered shale			Bentonite			No. 2 fire clay			N. Ca. kaolin			
Method of observation	Touch		Unrestricted	Touch		Unrestricted	Touch		Unrestricted	Touch		Unrestricted	Touch		Unrestricted	Basis of judgment
	(a)	(b)		(a)	(b)		(a)	(b)		(a)	(b)		(a)	(b)		
Observer (1)	3	3	1	2	2	2	1	1	3	4	4	5	5	5	4	Smoothness Drying speed
(2)	1	2	1	2	1	2	4	4	3	3	3	4	5	5	5	Cohesiveness
(3)	2	2	2	1	1	1	3	3	3	5	5	5	4	4	4	Yield
(4)	1	1	3	2	2	2	3	3	1	5	4	4	4	5	5	Yield Cohesiveness Adhesiveness
(5)	3	5	5	2	4	4	1	1	1	5	2	3	4	3	2	Cohesiveness
Adsorption (dye)	...	3	...	...	2	...	...	1	...	...	4	...	...	5	...	
Atterberg test	...	3	...	...	2	...	...	1	...	...	4	...	...	5		

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[1] Jour. Amer. Ceram. Soc., V, p. 474, 1922.

In the last vertical column is indicated the property on which the observer claims to have based his judgment.

It is quite evident that the different observers did not agree with each other, or with themselves. It is also interesting to note that the dye test and Atterberg test did agree with each other.

Test of clay in the dried condition.—Of the dry methods there are several. One suggested is the tensile strength test, based on the assumption that there is a direct relation between the tensile strength of the dry clay and its plasticity. The relation is only a general one, and there are many exceptions, in other words, the tensile strength does not vary directly as the plasticity.

Bischof [1] advocated the use of a set of mixtures of a standard clay with varying amounts of sand. Each of these is rubbed with the fingers, and the amount of dust that can be rubbed off is noted. The clay to be tested is similarly rubbed, and rated with one of the standard series which has lost a similar amount by rubbing. The method is crude and inaccurate.

TEXTURE

Definition.—By the texture of a clay is meant its size of grain or fineness, and since this exerts an important influence on the physical properties, such as plasticity, shrinkage, porosity, fusibility, etc., it should receive more than passing consideration. Many clays contain sand-grains of sufficient size to be visible to the naked eye, but the majority of the particles in clay are too small to be seen without the aid of a microscope, and are therefore so small that it becomes impossible to separate them with sieves.

Mechanical analysis.—In determining the texture of a clay, various methods of separation may be used, although it is perhaps of sufficient importance for practical purposes to determine the per cent of any sample that will pass through a sieve of 200 meshes to the inch. If it is desired to measure the size of all the grains found in the clay, some more delicate method of separation becomes necessary, and in order to do this it is essential that the mass of clay should be first thoroughly disintegrated.

This may be done by placing the clay in a stoppered bottle with water and a few drops of ammonium hydroxide, and putting it in a shaking machine. Here it is agitated until disintegration is complete.[2]

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[1] Die feuerfesten Thone, p. 88.

[2] U. S. Dept. of Agric. Bur. of Soils, Bull. 4, p. 9, 1896.

METHODS OF SEPARATION

A number of different methods have been devised for determining the texture of clays, but few of them are probably used to any great extent. They involve various principles such as separation by settling, by water currents, by wind, etc., and the majority require more or less special apparatus.[1]

In all water separations, the concentration of the clay-water suspension exerts an important influence on the results obtained.

G. W. Robinson [2] has called attention to the fact that suspension concentration not exceeding 5 per cent gives the best results, thus confirming Searle's statement that the water used should be twenty times the amount of clay.

Screen analysis.[3]—If clays contain sizes of larger diameter than 0.066 mm. (0.0029 in.) these can be separated by screens, but water has to be used to wash the finer grains through the mesh. After the residues on the different sieves are dried, the material should be rescreened, as particles which may not pass a given mesh when wet, will do so when dry.

The purpose of a fineness test, according to the American Ceramic Society specifications " is to so separate and classify that portion of a clay coarser than 0.0029 inch as to afford an index of its sandiness and contamination with coarse impurities. It is of further service in making it easier to judge the character of the coarse material by the removal of the fines. The 0.0029-inch sieve is sufficiently fine to detect the sand in clays which are in the least ' sandy ' as the term is ordinarily used."

The sieves recommended are those which conform to what is known as the Rittinger scale based upon an opening of 0.0029 inch in the 200-mesh size, with a wire 0.0021 inch diameter, the successive sieves having openings increasing in the ratio of the square root of 2 or 1.414.

At least two sieves shall be used, and if only two, those of 0.0082 and 0.0029-inch openings. If more than two are used they shall include these.

The clay is to be ground without crushing the sand particles. Three hundred grams are taken, dried at 110° C. and slaked in enough water to make a slip.

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[1] For a comparison of several of the methods see: Parmelee, Trans. Amer. Ceram. Soc., XI, p. 467, 1909; Darby, G. M., Chem. Met. Eng., XXXII, p. 688, 1925; Boswell, P. G. H., Trans., Faraday Soc., XVIII, p. 34, 1922; S. Oden, Soil Science, XIX, p. 1–37, 1925; Baker, H. A., Geol. Mag., LVII, pp. 363, 411, 463, 1920; Boswell, P. G. H., Memoirs on British Resources of Sands and Rocks Used in Glass Making, Longmans, Green & Co., 1918.

[2] Jour. Agric. Science, XII, p. 306, 1922.

[3] See Kerr, C. H., Note of Standard Testing Sieves, Trans. Amer. Ceram. Soc., XV, p. 375, 1913.

The sieves are dried, weighed, and the clay washed through them. After drying to constant weight, they are nested with cover attached, and shaken for one minute. They are then weighed individually with the sandy residue in each.

Settling method. Beakers.—A method known as the beaker method, and suggested by Whitney is simple, but somewhat inconvenient on account of the large amount of water required. Its operation is as follows:[1]

" The thoroughly disintegrated clay is transferred to a 3-inch beaker, which we may call *S*. This is filled with water and thoroughly stirred. It is then allowed to settle until all solid particles larger than 0.05 mm. have subsided. This is determined by taking a sample of the turbid liquid from near the bottom of the beaker by means of a small tube, transferring a drop of it to a microscope slide, and measuring the size of the particles.

" When the particles larger than 0.05 have subsided, the turbid liquid is carefully decanted into a larger beaker, *M*. This turbid liquid contains silt, fine slit, and clay, but no sand if the separation has been properly timed. The sediment in *S* consists of sand, containing still some silt, fine silt, and clay. This is stirred up with water and again allowed to settle until all the grains of sand have subsided, when the turbid liquid is again decanted into *M*. This operation is continued until an examination of the sediment in *S* shows that all particles smaller than 0.05 mm. have been removed. The contents of this beaker *S* are then washed into a small porcelain dish and evaporated to dryness on the water-bath. When dry this sand may be gently ignited to burn off the organic matter, and when cool it is sifted through a series of sieves which will be described further on.

" It is often convenient in separating the silt, fine silt, and clay from the sand to decant before the last portions of sand have settled. This hastens the operation of separating the fine and the coarse material, especially where there is a large mass of sand and but little fine material to be removed. In this case, the turbid liquid which is decanted is put into a separate beaker, and the sand which has been poured off is recovered by a further decantation, and when free from all fine material it is added to the sand in the porcelain dish while the latter is evaporating to dryness. The turbid liquid in the beaker *M* is thoroughly stirred and allowed to settle until a drop taken from near the bottom contains no particles larger than 0.01 mm. diameter. The liquid is then decanted into another beaker *P*. The sediment remaining in *M* is again stirred allowed to settle and decanted as before, continuing the operation until all particles smaller than 0.01 mm. have been removed. Wash the sediment from *M* into a dish, evaporate, ignite and weigh.

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[1] U. S. Dept. Agric., Bur. of Soils, Bull. 4, p. 10, 1896.

Stir up sediment in beaker *P*, then allow to settle until all particles larger than 0.005 mm. have subsided and decant turbid liquid into beaker *C*. Keep repeating until all particles smaller than 0.005 have settled and weigh the sediment in *C* after drying. The final suspension represents clay.

The sand separated in the beginning of the operation and dried and ignited in the porcelain dish is sifted through a series of sieves having openings of 2 mm., 1 mm., and 0.5 mm. diameter, respectively.

The passing through the lower sieve is then sifted through two grades of bolting-cloth—Nos. 5 and 13—having square holes approximately 0.25 and 0.1 mm. in linear dimensions.

Each of these grades of sand is weighed without previous drying, as the amount of hygroscopic moisture is usually inappreciable.

"The water used in the mechanical analysis should be distilled, if possible, but clear river, well, or hydrant water may be used. In case distilled water is not available, the solid matter in suspension or in solution in the water used should be determined by evaporating 500 c.c. of the water to dryness, and igniting and weighing the residue. Allowance should then be made for this residue in the clay determination.[1]

Bureau of Mines apparatus.—An apparatus designed by Bureau of Mines [2] to determine quantitatively the clay remaining in suspension at different intervals of time and subsequently the size of grain particles removed, is shown in Fig. 51. With this tube the liquid with most of the clay particles in suspension can be decanted. As, however, many of the particles due to momentum obtained while settling, fall below opening of drain tube they are not removed. They can only be removed by repeatedly adding distilled water, shaking, and decanting again. Thus to separate particles remaining in suspension at end of two days, the slip is thoroughly shaken, allowed to stand for that time, and then drained off by lifting the stopper from drain tube. The tube is then refilled and shaken and allowed to stand, the process being repeated until liquid is clear. Decantations can also be made at shorter intervals.

Weighing method.—Sven Oden [3] used an apparatus consisting of a glass cylinder, an automatic balance, and a recording apparatus. A movable plate, suspended from the balance by means of gold threads hangs directly over the bottom of the cylinder. The settling particles collect on the plate and the rate of sedimentation may be obtained by weighing the same at intervals.[1]

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[1] Modifications of this method have been used by: Beyer, S. W., and Williams, J. A., Ia. Geol. Surv., XIV, p. 119, 1903, and Searle, A. B., Chemistry and Physics of Clays, 1924; see also Stark, Phys. Tech. Untersuchung, Keram., Kaoline, Leipzig.

[2] Jour. Amer. Ceram. Soc., IV, p. 815, 1921.

[3] Soil Science, XIX, p. 1, 1925.

Elutriation method.—In this method as commonly understood the clay is treated with a current of water or sometimes an air current. The velocity of the current governs the size of the particles transported.

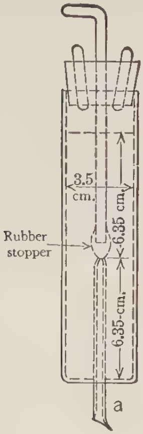

Fig. 51.—Apparatus to determine quantitatively clay remaining in suspension. (Jour. Amer. Ceram. Soc., IV, 1921.)

Schurecht in studying the fineness of clays by the elutriation method found that over one-half of the clays tested contained 50–100 per cent clay finer than 0.003 mm., and that it was impracticable to separate particles smaller than this by elutriation.[2]

The same fact has been noted by Schlosing,[3] Sven Oden,[4] and Wiegner,[5] all of whom used the sedimentation method for classifying very fine soil particles.

Schöne elutriator.—With this apparatus the clay after disintegration has the pebbles and coarse sand particles screened out. The finer portion is then placed in a tube (Fig. 52) where it is exposed to an upward current of water. Since the carrying power of the current increases with its velocity, a slow current will carry off only the finest particles, while the heavier ones remain behind. If the velocity is kept constant the water finally becomes clear. The current can then be increased sufficiently to carry off the particles of the next larger size and so on.

The apparatus consists (Fig. 52) of the separating funnel *A*, connected at the top with a narrow Z-shaped tube *K*, which has an opening at *L*, 1.5 mm. diameter. The clay is placed in *A*. Water is run in from the reservoir *D*, the supply being regulated by the stopcock *E*, thus insuring a definite velocity in *A*. The rapidity of flow depends on the quantity of water entering *A* per second. Knowing the amount of water and the cross section of *A*, the velocity is equal to the quantity divided by the cross section. The quantity is measured by allowing it to run into a measuring vessel for a definite length of time, care being taken that the level of the water in *K* remains constant. In this way the flow per second can be calculated.

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[1] See also Calbeck, J. H., and Harner, H. R., Particle size and distribution by sedimentation method, Ind. and Eng. Chem., XIX, p. 58, 1927; Robinson, G. W., Jour. Agric. Sci., XII, p. 306, 1922, and XIV, p. 626, 1924.

[2] Jour. Amer. Ceram. Soc., IV, p. 812, 1921.

[3] Comptes rend., CXXXVI, p. 1608, and CXXXVII, p. 369, 1904.

[4] Internat. Mitt. für Bodenkunde, V, p. 257, 1915; Bull. Geol. Inst. Univ. Upsala, XVI, p. 15, 1919.

[5] Die landwirtschaftlichen Versuchsstat., XCI, p. 41, 1918.

The velocity of the flow can be told by the height to which the water backs up in the tube *k*. This has to be determined in calibrating the instrument.

To every velocity there corresponds a size of grain determined by calculations, and five sizes are made, as follows:

1. Clay substance, including particles removed by a flow of 0.18 mm. per second. Maximum diameter 0.01 mm.
2. Silt, including grains removed by a flow of 0.70 mm. per second. Maximum diameter 0.025.
3. Dust-sand, including particles removed by a flow of 1.5 mm. per second. Maximum size 0.04 mm.
4. Residue remaining in funnel, called fine sand. Diameter 0.04 to 0.2 mm.
5. Coarse sand, everything larger than 0.2 mm.

An objection to the apparatus is its fragility, the large volume of water used, and time required to run[1] an analysis.

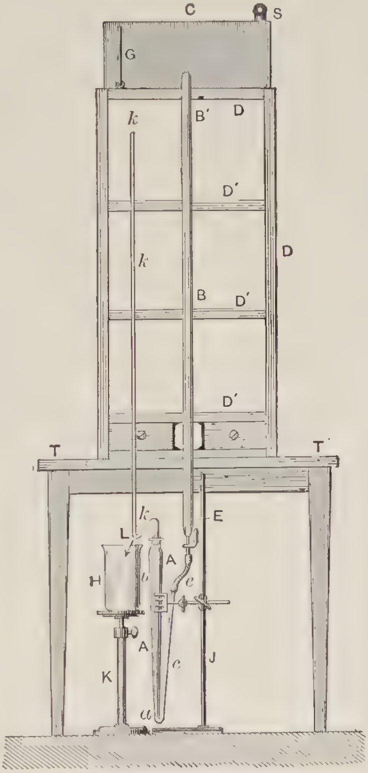

FIG. 52.—Schöne's apparatus for elutriation of clay.

Hilgard's elutriator.—A form of apparatus devised by E. W. Hilgard (Fig. 53), is a modification of the preceding. It has a revolving paddle at the base of a cylindrical tube, which is supposed to eliminate the counter currents developed in the Schöne apparatus. Its operation otherwise is similar.

Schurecht-Schulze elutriator.—Another modification of the Schulze elutriator has been proposed by Schurecht.[1] He uses a 500-gram sample, crushed to pass a 4-mesh sieve, after which it is thoroughly blunged with 1000 c.c. distilled water in a two-quart "Daisy" churn. The clay is then wet-screened to separate the different sizes above 200 mesh. The fine clay-water mixture is fed drop by drop into the elutriator, and ammonium hydroxide is introduced into the feed water through a side funnel. A special feature is that the overflow passes over the rims of the cans and is caught in a launder which extends around the outside. Before introducing a sample into the elutriator the rate of flow is reduced about one-third. The apparatus has to be carefully standardized beforehand, and details of this are given in Schurecht's paper referred to below.

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[1] For other references on Schöne apparatus see: Jackson, W., Trans. Ceram. Soc. (Eng.), III, p. 16, 1903–4; Mellor, J. W., Trans. Ceram. Soc. (Eng.), XVIII, p. 252, 1918–19; Mayer, E., Trans. Amer. Ceram. Soc., IV, p. 25 (Results of tests on ground flint); Seger, H., Collected Writings, I, p. 44, 1902.

The apparatus gives close checks if care is used, and the observed diameter of the particles, as separated with distilled water, correspond closely to the calculated results obtained by using Schöne's empirical formula.[2]

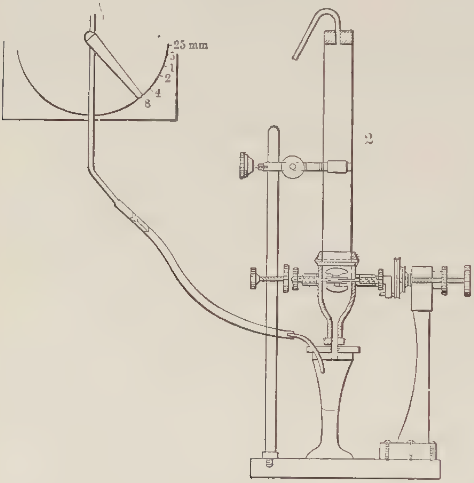

Fig. 53.—Hilgard's apparatus for making mechanical analyses.

Krehbiel elutriator.—A type of separator which is a modification of Schultz's, but seemingly possessing several advantages, and being at any rate cheaper to construct, is that suggested by Krehbiel.[3] It consists essentially of three cylinders with cone-shaped bottoms placed at different heights (Fig. 54), so that the overflow from the first flows through the thistle tube to the bottom of the second, and so from the second to the third. The water supply is constant coming from a tank with an overflow and fed from a faucet. The height of the tank depends on the opening in the end of the delivery tube, and is adjusted by trial. The cylinders have different diameters to produce a separation of the particles according to the following sizes, namely, in the first or smallest can: particles 0.12 mm. to 0.04 mm.; in the second can: those 0.04 mm.

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[1] Jour. Amer. Ceram. Soc., III, p. 355, 1920.

[2] For other references see Jackson and Purdy, Trans. Ceram. Soc. (Eng.), IX, p. 110; Watts, U. S. Bur. Mines, Bull. 53, p. 46.

[3] Trans. Amer. Ceram. Soc., VI, p. 173, 1904.

to 0.025 mm.; and in the third, 0.025 mm. to 0.01 mm. The overflow consists of particles smaller than 0.01 mm.

Whirlpool classifier.—Stull and Bole found that if instead of discharging the slip into the can as was done in the Schurecht elutriator, it was allowed to flow in tangentially from a constant head, there was set up a whirlpool motion. This caused the coarser particles to be carried towards the center and downwards, where they are collected. The fine clay particles and water float out over the top of the can. Greater efficiency is said to be obtained with this apparatus than is possible with a simple elutriation process.[1]

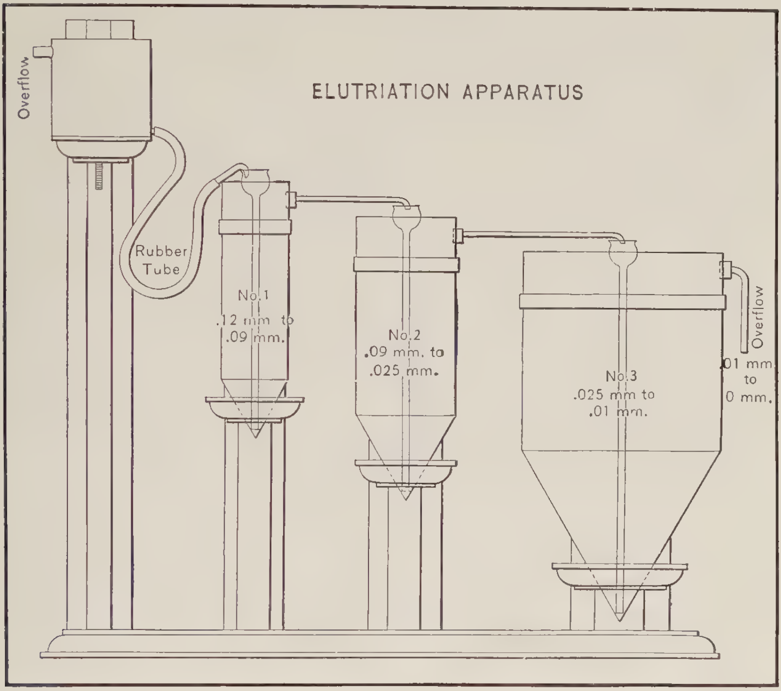

Fig. 54.—Krehbiel's elutriator for mechanical analysis of clay. (Krehbiel, Trans. Amer. Ceram. Soc., VI, 1904.)

Air elutriator.[2]—This form of apparatus was devised in order to overcome the defects of any wet method of separation. "The apparatus (Fig. 55) consists of five percolating jars set in a wooden frame and connected by tubes of glass passing through close-fitting caps tightly clamped to the jar tops. The first jar is of 3 gallons capacity, the second 2 gallons, and the remaining ones of 1 gallon each. In the bottom of No. 1 is placed a flat spiral tube closed at one end, but with a number of very small openings through small jets soldered into the upper surface of the spiral at an angle of about 30°. The open end of the spiral passes through a tightly fitting rubber stopper inserted in the neck of the jar and is connected to the source of air supply. An inverted funnel tube whose stem passes through another rubber stopper fitted in the cap at the top of the jar is connected to a glass tube which passes in a similar manner nearly to the bottom of No. 2. An inverted thistle tube connects No. 2 with No. 3 in like manner, and so on through Nos. 4 and 5, the exit tube of No. 5 being connected to a vacuum. The exit of No. 5 was covered with fine linen lawn. Rubber stoppers close the necks of the jars and are removed only when it is desired to draw off the charges of powder which have accumulated during a run. A charge of oven-dried powder not exceeding 1 kilogram is placed in jar No. 1. Blast and vacuum are then turned on and adjusted so that a steady stream of air passes through the powder with sufficient force to raise a dense white cloud, which assumes a vortex motion as it ascends, owing to the arrangement of the air jets. The heavier particles continually fall in a ring near the walls of the vessel, where they build up

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[1] Jour. Amer. Ceram. Soc., VI, p. 731, 1923.

[2] A. S. Cushman and P. Hubbard, Air Elutriation of Fine Powders, Jour. Amer. Chem. Soc., XXIX, No. 4, Apr., 1907.

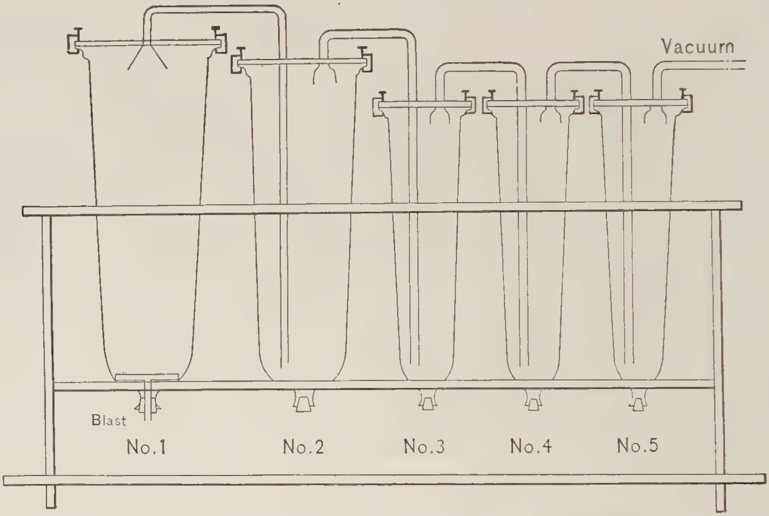

Fig. 55.—Cushman's air elutriator. (After Cushman and Hubbard, Jour. Amer. Chem. Soc., XXIX, No. 4.)

until caved in by the air jets, while the lighter particles are carried into No. 2 through the funnel tube, and so on, the very finest being caught in the last jar."

Other separation methods.—In addition to the simple settling and current methods of separation, several others have been used as described below.

Centrifugal separator.—This is perhaps one of the most satisfactory methods that has been devised. It consists (Fig. 56) of a fan motor[1] placed with the armature shaft in a vertical position. This carries a framework with eight test-tube holders, trunnioned, so that they can swing outwards and upwards as the frame revolves.

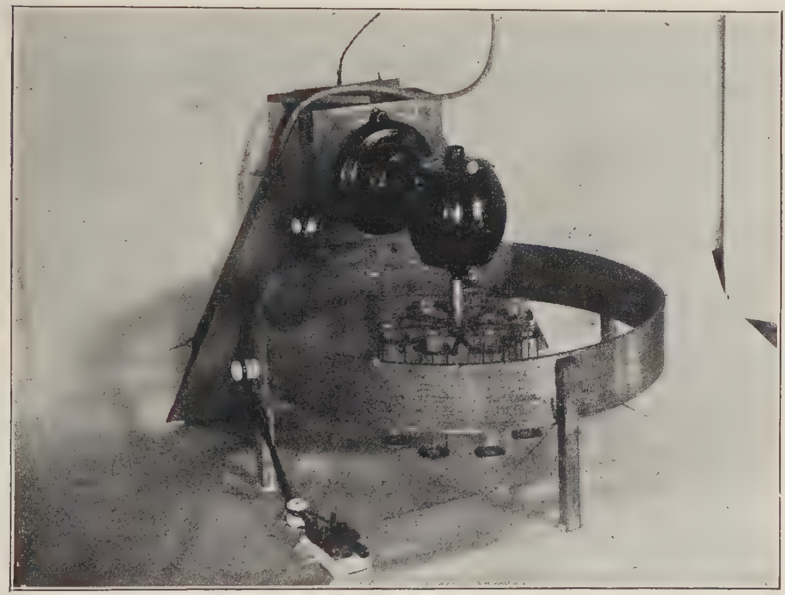

FIG. 56.—Centrifugal separator for mechanical analysis. (Photo loaned by Bureau of Soils.)

The disintegrated sample is placed in these tubes, and twirled at a high speed for several minutes. As a result of this all particles except the finest clay grains are thrown to the bottom of the tube by centrifugal force. These are decanted off, the tubes refilled with water, and the sediment again stirred up. A second twirling of the tubes, either at a lower speed or for a shorter period, precipitates everything except the fine silt, which is then also decanted off. The subsequent sizes are then separated from each other partly by settling and partly by sieves.

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[1] U. S. Dept. Agric., Bur. Soils, Bull. 64, 1900.

The different sizes which can be so separated and their dimensions are shown in the table below:

TABLE SHOWING SIZE OF GRAINS OF SAND, SILT, AND CLAY

Conventional name	Size of diameters	
	Inch	Millimeters
1. Gravel	1/12 –1/25	2–1
2. Coarse sand	1/25 –1/50	1–0.5
3. Medium sand	1/50 –1/100	0.5–0.25
4. Fine sand	1/100 –1/250	0.25 –0.1
5. Very fine sand	1/250 –1/500	0.1 –0.05
6. Silt	1/500 –1/2500	0.05 –0.01
7. Fine silt	1/2500–1/5000	0.10 –0.005
8. Clay	1/5000–1/25000	0.005–0.0001

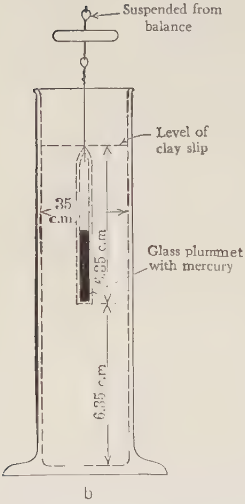

FIG. 57.— Plummet sedimentation apparatus. Jour. Amer. Ceram., Soc. IV, 1921.

Plummet apparatus.[1]—This consists of a plummet, a closed glass tube half-filled with mercury, suspended from a chemical balance by means of a thin copper or gold thread (Fig. 57). Since the suspended weight is greater with a low clay content than with a high one, the specific gravity variation of the upper half of the slip may be calculated from the suspended weights of the plummet. This method for determining specific gravities is said to be accurate to 0.0001 g./c.c.

In operation the cylinder is filled to a level equal to 12.70 cm. above bottom when plummet is in place, and is then thoroughly shaken and placed beneath the balance. The plummet is slowly lowered into slip, weighed, and the time of starting test and making weights recorded. Weighings are repeated at intervals of 1, 2, 3, 5, 10, 20, 35, and 60 minutes; 2, 3, 5, and 7 hours, and 1, 2, 3, 5, 10, 20, and 30 days. The number of weighings depends on the clay, few particles remaining in suspension after five days.

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[1] Schurecht, H. G., Jour. Amer. Ceram. Soc., IV, p. 816, 1921.

After first seven hours, the cylinder is kept stoppered and the plummet is lowered into the suspension for each weighing. This permits the same plummet to be used for a number of cylinders. The temperature of liquid should be kept uniform.

Since different clays have different specific gravities and different shaped grains, the size of particles remaining suspended after different intervals may be determined by catching a drop of the liquid adhering to plummet each time it is removed, and examining same under microscope.

The clay remaining in suspension may be determined from

$$S = \frac{Pd - Ps}{Pd - Pw} = \frac{\text{Weight of slip equal to volume of plummet}}{\text{Weight of water equal to volume of plummet}}.$$

S = Specific gravity of slip;
P = Dry weight of plummet in grams;
Pw = Suspended weight of plummet in distilled water in grams;
Ps = Suspended weight of plummet in slip in grams.

Since $Pd - Pw$ is constant for each plummet, the values of S for different volumes of $(Pd - Ps)$ may be plotted on a chart as a straight line. With this chart the values of S may be readily obtained from $Pd - Ps$.

The average weight of clay per cubic centimeter is then obtained from the formula

$$Cw = \frac{D(S - d)}{D - d}.$$

Cw = Average weight of clay per cubic centimeter of slip;
D = Specific gravity of clay;
d = Specific gravity of water;
S = Specific gravity of clay slip.

Assuming that $d = l$ for water, the following formula is obtained:

$$Cw = \frac{D(S - 1)}{D - 1}.$$

Since D is constant for a given clay, the values of Cw for different values of S may be plotted on a chart as a straight line. With this chart the values of Cw may be readily obtained. Since the specific gravity of a clay may vary between 2.5 and 2.7, this should be determined for each sample.

One advantage claimed for the plummet apparatus is that it the separation of the extremely fine particles, below 0.003 r easier to keep at a uniform temperature, and keeps the electroly stant. It is also much more rapid than the sedimentation test.

Microscopic method.—A method for determining the text microscopic examination is described by G. St. J. Perrott an Kinney[1] as follows:

"A sample is mounted in Canada balsam, diluted with about cent xylol. A few drops of this mixture are placed on a piece dow glass and amount of pul coal[2] sample with it until tl ticles are even seminated in th sam. Two slide 75 mm. used for ing the sampl drop of the mix Canada balsam coal is placed clean slide. Tl in this mixture weigh about 0.0 A second thin placed on top drop and the slides gently pressed together and slid back an until there is an even distribution of coal and balsam. The r should cover a circular space about two inches in diameter.

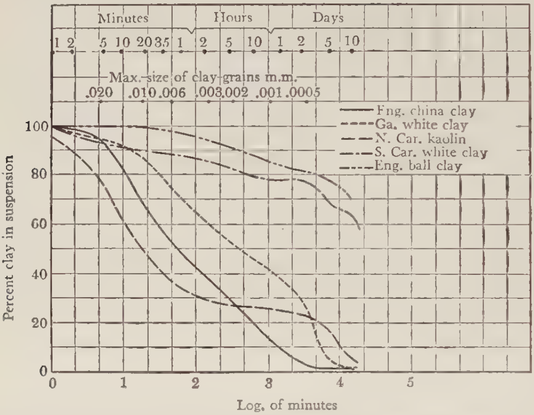

FIG. 58.—Results of sedimentation tests made by plummet method. Jour. Amer. Ceram. Soc., IV, 1921.

"The microscope is provided with a micrometer eyepiece, the est divisions of which are 10 microns at a magnification of 200 dia and $4\frac{1}{2}$ microns at a magnification of 500 diameters. A magnif of 200 diameters is usually employed.

"In making the determination, the microscope is first focused area at one corner of the slide and the total number of particl quarter field counted, making note of the size of each particle. work the 'size' or 'diameter' of the particle has been taken side of a square having similar area. This 'squaring' of the particle is carried out visually with the aid of the squared ruling of the eyepiece. Such procedure is approximate but probably gives values as nearly correct as any method can give on the irregularly shaped particles.

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[1] Jour. Amer. Ceram. Soc., VI, p. 417, 1923.

[2] The authors used the method in examining powdered coal, but it is ap to clays, etc.

"In making this count particles are grouped as being 1, 2, 5, 10, 15, 20, 30, 40, etc., microns in diameter. Our practice has been to count the number of largest particles first.

"Sufficient areas are examined so that a fair average of the number of particles of each size in a quarter field is obtained. For a sample of coal which has passed through a 200-mesh screen, this will entail estimation of the number of particles 2 and 5 microns in diameter in about 10 areas, 10 and 15 microns in diameter in some 40 areas, 20 and 30 microns in diameter in some 100 areas, while as many as 300 separate areas may have to be examined for a correct estimation of the average number of particles 40 microns or over."

Calculation.—An example of the method of calculation is given below:

Diameter in microns	Average number of particles in a quarter field		Relative weight	Per cent by weight		Micron
20	1	1×20^3	8,000	11.1	0.111×20	2.2
15	3	3×15^3	10,125	14.1	0.141×15	2.1
10	40	40×10^3	40,000	55.6	0.556×10	5.6
5	110	110×5^3	13,750	19.2	0.192×5	1.0
		Total rel. wt.	71,875	100.0	Aver. size	10.9

Relation between composition and texture.—Few analyses have been published showing the chemical composition of the different-sized grains in a clay.

G. P. Grimsley and F. F. Grout have analyzed the mechanical separations of sixteen samples of clay with the following results:[1]

[1] W. Va. Geol., III, p. 61, 1906.

Size in mm.	I	II	III	IV	V
SiO_2	44.08	54.24	70.30	81.16	73.63
Al_2O_3	28.16	23.00	16.04	9.76	13.01
Fe_2O_3	7.94	5.91	3.21	2.13	4.71
FeO	.99	.99	.63	.40	.18
CaO	.76	.82	.72	.31	.47
MgO	1.36	1.02	.80	.39	.48
K_2O	3.05	3.31	2.14	1.78	.93
Na_2O	.00	.29	.45	.56	.00
Moist	2.80	1.10	.56	.35	.87
Ignition loss	10.86	7.79	4.33	2.59	4.40
TiO_2	.84	1.12	1.08	.78	.60

I. 00 to 0.001.
II. 0.001 to 0.005.
III. 0.005 to 0.02.
IV. 0.02 to 0.15.
V. 0.15 up.

As might be expected these analyses show a higher percentage of silica in the coarser grains, still the increase is not a steady one, but none of the other ingredients show either an increase or decrease from coarse to fine. The maxima are in each case underscored. The appreciable titanium percentage in even the coarser grains is of interest, although it is not known in what form the titanium occurs therein.

Analyses of twelve Minnesota clays separated mechanically into five fractions, each of which was analyzed, showed that silica tends to concentrate in the sand while Al_2O_3, Fe_2O_3 and K_2O tend to concentrate in the silts and clays. The CaO, MgO and Na_2O vary erratically. Kaolinite and ferric minerals are more abundant in the finer sizes, while quartz and carbonates are said to be less abundant.[1]

Fineness factor.—The fineness of ground materials used in the ceramic industry is frequently expressed by means of a term known as the surface factor.[2] The factor often used is that of Jackson as modified by Purdy. It is based on the assumption that the surface areas of two powders, derived from a unit volume are in inverse ratio to the average diameter of their grains, and hence the reciprocal of the average diam-

[1] Grout, F. F., Bull. Geol. Soc. Amer., XXXVI, p. 393, 1925.

[2] See Jackson, Trans. Eng. Ceram. Soc., III, p. 16; Krehbiel, Trans. Amer. Ceram. Soc., VI, p. 173, 1904; Binns, Trans. Amer. Ceram. Soc., VIII, p. 244, 1906; Purdy, Trans. Amer. Ceram. Soc., VII, Pt. III, p. 441, 1905; Cushman and Hubbard, Jour. Amer. Chem. Soc., XXIX, No. 4, 1907.

eter is taken as the factor. Although the assumption is in error,[1] the factor affords a convenient approximation, and is often used. The Purdy factor is obtained as follows: The elutriation of a powder is supposed to have separated it into the four following sizes: No. 1, diameters ranging from 0.12 to 0.04 mm.; No. 2, 0.04 to 0.025 mm.; No. 3, 0.025 to 0.01 mm.; No. 4, 0.01 to 0.00. Taking the average diameters the surface factor of each group is as follows:

Group	Average diameter	Surface factor	Per cent present
1	0.080	$\frac{100}{8} = 12.50$	10
2	0.0325	$\frac{10000}{325} = 30.77$	20
3	0.0175	$\frac{10000}{175} = 57.14$	20
4	0.0050	$\frac{10000}{50} = 200.00$	50

The total surface factor is obtained by multiplying the surface factor of each size by the percentage weight of each group, and finding the sum of the products thus obtained. Thus:

$$\begin{array}{rr} 12.50 \times & 0.10 \\ 30.77 \times & 0.20 \\ 57.14 \times & 0.20 \\ 200.00 \times & 0.50 \\ \hline & 118.83 \end{array}$$

Strength of Dry Clay[2]

The strength of a dry clay is an important property and has a practical bearing on problems connected with the handling, molding, and drying of the ware, since a high strength enables the clay to withstand the shocks and strains of handling. Through it, also, the clay is able to carry a large quantity of non-plastic material, such as flint, feldspar, ground bricks, etc.

The strength of a dry clay may be determined by the transverse, tension, or compression test. Formerly the tensile strength was the property commonly determined, but now the transverse strength test is usually employed, because it gives more uniform results. Compressive tests are rarely used.

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[1] Cushman and Hubbard, l. c.

[2] For further information on this subject see the following articles in Trans. Amer. Ceram. Soc., VII, pp. 397, 195; XII, p. 141, 1910; XV, pp. 271 and 345, 1913; XVI, p. 277, 1914; XVII, pp. 92, 412 and 651, 1915; XIX, p. 603, 1917; N. J. Ceramist, Mar. 1922, p. 5; Brit. Clayw., XXXII, p. 293, 1924.

TRANSVERSE STRENGTH

The transverse strength is the resistance which a bar of clay offers to a load applied at right angles to its length.

This test is made by molding the clay into a bar, and after thorough drying determining its cross-breaking strength in terms of the modulus of rupture (R), calculated from the formula.

$$R = \frac{3wl}{2bh^2}.$$

w = weight required to break bar;
l = distance between supports;
b = width of bar;
h = height of bar.

It is of great importance that the bars should be carefully molded and gradually as well as thoroughly dried.

An apparatus for making the transverse test is shown in Fig. 59.

The specifications for the test as recommended by the American Ceramic Society are as follows:

" The clay shall be thoroughly dried at 65° C. or above, but under 100° C., crushed and screened to pass a standard 28-mesh sieve (0.0232″ hole, 0.0125″ wire). It shall then be thoroughly mixed dry with 50% by weight of standard silica sand that passes a 20 mesh (0.0328″ hole, 0.0172″ wire) and is retained on a 28 mesh (0.0232″ hole, 0.0125″ wire) standard sieve. The mixture shall then be made up to soft-mud consistency with water and thoroughly pugged by hand.

" The test piece shall be made in a suitable metal or wood mold. It shall be 7″ long and have a 1″ square cross section in the plastic state.

" The mold shall be evenly and thinly oiled with kerosene and placed on a firm smooth surface. A lump of the clay mixture, somewhat larger than is required to fill the mold, shall be thrown forcibly into the mold so as to completely fill out the lower corners. The excess shall then be cut off with a spatula, and the top slicked off and appropriately marked.

" The test pieces shall be allowed to dry in room temperature until air dry. They shall then be placed in a drier operating between 65° and 75° C. for at least five hours, and from there transferred to a drying oven, operating at 110° C., where they shall remain until approximately constant in weight.

"The test pieces shall be cooled in a desiccator and then measured in breadth and thickness in hundredths of an inch, each being the average of two readings. They shall then be broken in a suitable machine, having knife edges with a $\frac{1}{4}''$ radius and $5''$ apart. The machine should have an automatic shutoff for the shot, and the rate of loading should be about 100 lbs. per minute.

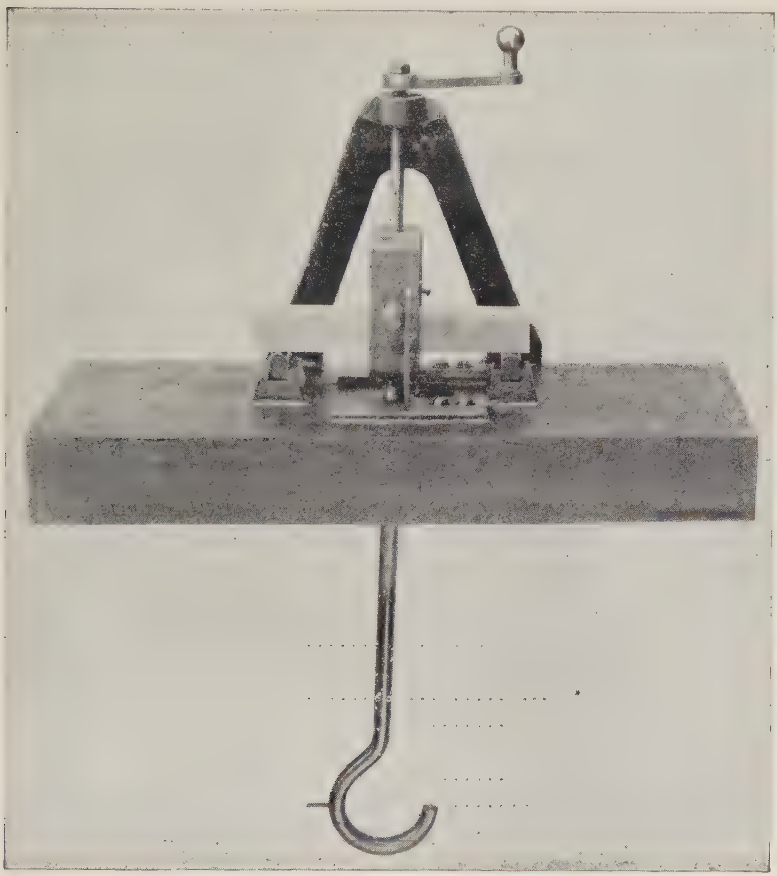

FIG. 59.—Apparatus for testing the transverse strength of clays. A shot pail is hung on the hook, and shot fed into it from shot box with automatic shut off.

"The modulus of rupture shall be calculated by the formula given above. The average of 10 test pieces shall constitute a test except that two faulty test pieces are allowable, in which case the average shall be taken of the eight or nine remaining.

"A variation of plus or minus 15% from the average modulus of rupture is permissible. The test pieces showing a greater variation shall be considered faulty and discarded."

Range of transverse strength.—The modulus of rupture of dried clays shows a remarkable range, running from a few pounds per square inch in some kaolins up to 1500 lbs. in some very plastic clays.

No standard terms have been adopted, but Watts[1] suggests the following:

	Pounds
Low	0–100
Medium low	100–200
Medium	200–400
Medium high	400–800
High	Over 800

Transverse strength of different clays.—The following range is shown by different types of clay, the figures being taken chiefly from a number of published sources.

Type of clay	Modulus of rupture
Washed kaolin	75– 200
White sedimentary kaolin, Ga.-S. Ca.	150– 166
Ball clay	25– 600
Crucible clay	187– 691
Refractory bond clay	395–1093
Glass pot clay	173–1068
Sagger clay	46– 474
Stoneware clay	94– 678
Sewer-pipe clay	190– 589
Brick clay	50–1500

Effect of moisture content.—A rather interesting series of figures has been given by C. H. Kerr and R. J. Montgomery.[2]

Working with St. Louis fire-clay alone (*a*), and a mixture of the same with 50 per cent grog (*b*), it was found that: (1) The maximum strength

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[1] Jour. Amer. Ceram. Soc., VI, p. 247, 1920.

[2] Trans. Amer. Ceram. Soc., XV, p. 270–8.

(modulus of rupture) was reached only when the bars were dried to less than 1 per cent moisture for (*a*) and 0.5 per cent moisture for (*b*); (2) the maximum strength of both (*a*) and (*b*) was not attained until long after all shrinkage was over; (3) when shrinkage was completed only about half the maximum strength was attained; (4) with (*a*) no measurable strength was obtained until the water was reduced from 26.6 per cent (best plasticity) to 20 per cent. With decrease from 20 to 11 per cent the modulus of rupture increased regularly from 0 to 300 lbs. per sq. in. From 11 per cent to 3 per cent water there was no change in strength. Below 3 per cent the strength increased rapidly to 600 lbs. at 0.5 per cent water; and (5) with (*b*) starting at 17.6 per cent water there was a maximum point on the strength curve at 8 per cent water (165 lbs. per sq. in.). Below 1.5 per cent water the strength increased rapidly to 300 lbs. at 0.1 per cent water.

The details of these tests are given in the following table:

TRANSVERSE TESTS ON ST. LOUIS FIRE-CLAY

Modulus of rupture changes during drying							
St. Louis fire clay				50 per cent St. Louis fire clay; 50 per cent grog			
Per cent of water based on dry weight	Modulus of rupture, pounds per square inch	Length of shrinkage, per cent	Method of drying	Per cent of water based on dry weight	Modulus of rupture, pounds per square inch	Length of shrinkage, per cent	Method of drying
26.6	....	....	At start	17.6	....	....	At start
18.8	26	2.8	Air-dried	15.0	....	1.0	Air-dried
18.3	43	3.2	Air-dried	13.2	....	2.1	Air-dried
16.4	82	4.8	Air-dried	12.3	70	3.0	Air-dried
14.8	173	5.7	Air-dried	10.0	129	4.0	Air-dried
10.9	309	7.7	Air-dried	8.0	166	4.6	Air-dried
10.2	265	8.3	Air-dried	7.4	150	4.9	Air-dried
9.9	243	7.8	Air-dried	7.0	157	5.0	Air-dried
8.2	311	7.8	Air-dried	6.3	138	4.8	Air-dried
7.8	264	7.8	Air-dried	5.5	146	5.2	Air-dried
3.2	330	7.8	Over sulphuric acid	3.4	136	4.8	Air-dried
2.1	422	8.1	Over sulphuric acid	2.1	138	4.8	Air-dried
1.0	558	7.8	Over sulphuric acid	0.9	168	5.0	Air-dried
0.5	645	8.2	Over sulphuric acid	0.9	225	4.6	Over sulphuric acid
	303	7.8	Over sulphuric acid	0.1	271	4.9	Over sulphuric acid

Effect of sand.—The addition of sand usually decreases the transverse strength, although in some clays the reverse happens. The latter may be particularly true of some very plastic, fine-grained clays, which have a high air-shrinkage, as a result of which minute cracks are developed which act as flaws.

The following figures by A. V. Bleininger and W. L. Howat[1] show the effect of adding sand to a number of clays:

TRANSVERSE TESTS OF CLAY WITH AND WITHOUT SAND

	Modulus rupture, pounds per square inch	
	Without sand	With sand
Ball clays	375–588	242–330
Plastic fire-clay	484–520	216–280
Shales	311–403	178–237
Plastic kaolins	239–325	122–210
Primary kaolins	74–166	53– 82

TENSILE STRENGTH

The tensile strength of a clay is the resistance which it offers to rupture, or being pulled apart when air dried.[2]

Measurement of tensile strength.—The tensile strength is measured by molding the thoroughly kneaded clay into briquettes, of similar form and shape to those made for testing cement, and then when thoroughly dried in air, and at 105° C., pulling them apart in a suitable testing machine. The cross section of the briquettes when molded is 1 sq. in., but after drying it will be somewhat less than this depending on the air-shrinkage of the clay. Care should be used in filling the mold to see that the clay is uniformly pressed into it.

Not less than ten or twelve briquettes of each clay should be tested in order to obtain a fair average. Most clays should not show a variation of more than 15 or 20 per cent, but in clays of high strength it may be greater than this.

Any standard type of machine (Fig. 60) can be used for determining the tensile strength, but since there is sometimes a tendency for the jaws of the clip to cut into the clay, some asbestos, pasteboard, or rubber should be put between the inner surface of the clip jaws and the sides of the briquette.[3]

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[1] Trans. Amer. Ceram. Soc., XVI, p. 272, 1914.

[2] For relation of transverse to tensile strength see Ries, H. and Allen, S. W., Trans. Amer. Ceram. Soc., XII, p. 141, 1910.

[3] For a simple type of testing machine see Bleininger, A. V., and Howat, W. L., Trans. Amer. Ceram. Soc., XVI, p. 275, 1914.

The tensile strength is expressed in pounds per square inch, but since the clay shrinks in drying, allowance must be made for this, and the cross section measured before testing.

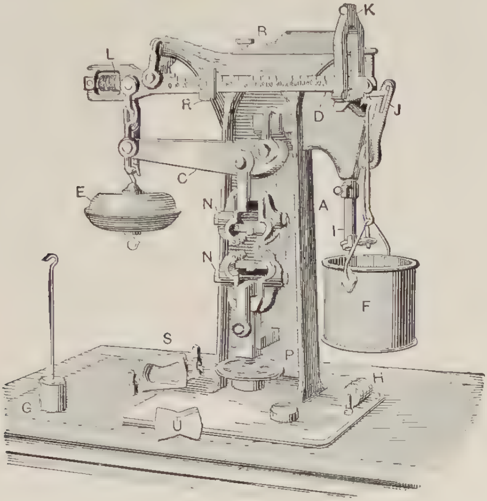

Fig. 60.—Fairbanks tensile-strength machine. *N*, clips for holding briquettes; *P*, screw for applying strain to balance-lever *C*; *F*, bucket to hold shot fed in through *I* from the hopper *K*; *J*, automatic cut-off.

Effect of drying on tensile strength.—The following figures by C. W. Saxe and O. S. Buckner[1] show the effect of thorough drying on the tensile strength:

Effect of Thorough Drying on Tensile Strength

Clay	I	II	III	IV
Ball clay	57.5	59.4	63.4	130.5
Ball clay	32.9	34.9	38.7	69.8
Ball clay	30.1	32.5	35.4	65.8
Plastic clay	65.3	69.9	77.1	107.4
Ball clay	49.7	52.1	54.5	85.5
Plastic clay	58.9	59.8	54.4	83.3
German crucible clay	64.1	70.6	76.1	87.9
American crucible clay	52.6	61.2	62.0	107.2
Slip clay	46.1	51.2	57.3	79.2

I. Air dried
II. At 55° C., 24 hours.
III. At 110° C., 24 hours.
IV. At 110° C., cooled in desiccator.

[1] Jour. Amer. Ceram. Soc., I, p. 113, 1918.

Range of tensile strength.—The following figures taken from various sources give the range in tensile strength shown by a number of different types of clay.[1]

RANGE OF TENSILE STRENGTH IN DIFFERENT KINDS OF CLAY

Type of clay	Tensile strength, pounds per square inch
Crude kaolin	50–100
Ball clay	33–200
Crucible clay	123–124
Refractory bond clay	95–132
Glass pot clay	59–227
Plastic fire clay	41– 65
Face brick lay	196–293
Paving brick clay	57–318
Brick clay	64–513

Cause of tensile strength.—In order to get satisfactory and reliable results, great care is necessary in molding and drying the briquettes, it being claimed by some that fine-grained clays will show an abnormally low strength unless dried very slowly.

Experiments by Orton [2] seem to bear out this fact. Five series of the same clay were tested by him as follows:

Series	Rate of drying	Average tensile strength, pounds per square inch
1	Quickest, severest drying	182.49
2	Somewhat slower	178.17
3	Still slower	176.13
4	Very slow indeed	204.80
5	Artificial conditions	205.53

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[1] For additional tests see Wheeler, H. A., Mo. Geol. Surv., XI, p. 111, 1897 Beyer, S. W., and Williams, I. A., Ia. Geol. Surv., XIV, p. 83, 1904; Ries, H., N. J Geol. Surv., Fin. Rept., VI, p. 85, 1904.

[2] Trans. Amer. Ceram. Soc., Vol. III, p. 202, 1901.

The fifth series was placed in a tightly closed jar with calcium chloride.

With such a variation existing in the tensile strength of clays, it becomes a matter of interest to know the cause of this variation. It is a well-known fact that all clays shrink in drying, and that this shrinkage is accompanied by a drawing together of the particles. Indeed, some clays shrink to such a hard mass as to suggest a close interlocking of the grains, which, it seems to the writer, may be the explanation of the tensile strength shown; that is to say, those clays in which the interlocking of the particles is the tightest will show the highest tensile strength and vice versa. If this is true it becomes necessary to determine, if possible, what arrangement or size of particles produces the tightest and strongest structure.

E. Orton, Jr.,[1] attempted to determine the effect of the fineness of grain on the tensile strength of clays by taking a very fine-grained clay and mixing different sizes of sands with it, the sand being obtained by grinding and screening vitrified bricks. His conclusions were " (1) that the tensile strength of mixtures of a plastic ball-clay with equal quantities of non-plastic sands will vary inversely with the diameter of the grains of the sand from grains of 0.04 inch down to the finest sizes obtainable. (2) That the non-plastic ingredients of clay influence its tensile strength inversely as the diameter of their grains, and fine-grained clays will, other things being equal, possess the greatest tensile strength." In other words, the coarser the grains of sand the less the tensile strength of the mixture containing them.

The results of these tests are shown graphically in Fig. 61.

A series of tests on natural mixtures of varying texture were undertaken by the writer in connection with a study of the New Jersey clays.[2] Five samples were selected at random as follows:

1. A very plastic, slightly gritty, dense, red-burning clay from the Alloway formation, with an average tensile strength of 453 lbs. per square inch.

2. A Pleistocene clay of gritty, plastic character, but not as dense as the previous one. Its average tensile strength was 297 lbs. per square inch.

3. A gritty, plastic clay from the Cape May formation, with an average tensile strength of 289 lbs. per square inch.

4. A Raritan clay of black color and sandy, micaceous character, with an average tensile strength of 105 lbs. per square inch.

5. A soft, powdery, washed ball-clay from the Raritan. It was

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[1] Transactions American Ceramic Society, Vol. II, p. 100, and Vol. III, p. 198.

[2] N. J. Geol. Surv., Final Report, Vol. VI, p. 87, 1904.

plastic to the feel, with very little grit, and a tensile strength of under 20 lbs. per square inch.

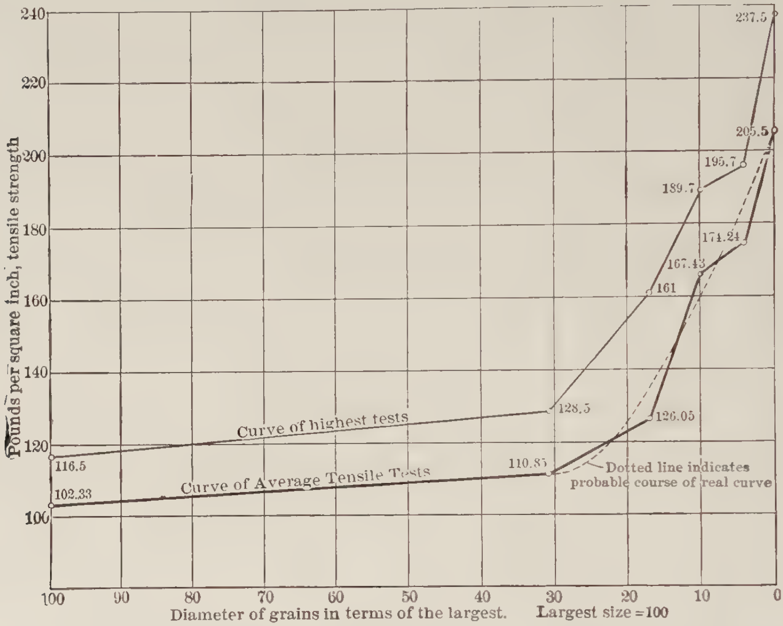

FIG. 61.—Curve showing relation between fineness of grain of non-plastic material and tensile strength of clay mixtures. (After Orton, Trans. Amer. Ceram. Soc., III.)

The percentage of the sizes in each of the five samples is shown in the following table:

MECHANICAL ANALYSES OF SOME NEW JERSEY CLAYS

Conventional names	I	II	III	IV	V
Clay substance	59.00%	44.00%	22.00%	30.645%	87.96%
Fine silt	11.00	7.11	5.66	14.21	6.95
Silt and fine sand	14.70	24.35	26.55	5.585	3.00
Medium sand	3.50	7.80	11.45	6.400	1.00
Sand	11.40	16.35	33.44	42.950	
	99.60	99.61	99.10	99.790	98.91

I. Laboratory No. 680.
II. Laboratory No. 659.
III. Laboratory No. 645.
IV. Laboratory No. 615.
V. Laboratory No. 723.

These figures seem to throw some light on the relation of the texture to the tensile strength, but, while highly suggestive, are not to be taken as final. The results of these tests are also shown graphically in the table (Fig. 62), in which the horizontal lines represent percentages. Of the six columns, the first five represent the grain sizes and the sixth the tensile strength.

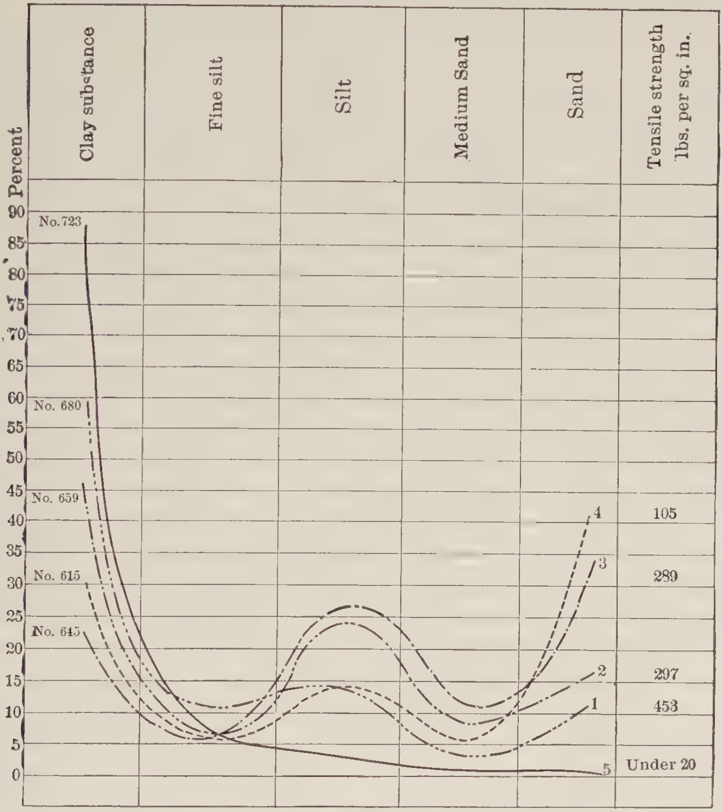

FIG. 62.—Curves showing relation of texture to tensile strength. (After Ries, N. J. Geol. Surv., Fin. Rept., VI, p. 89, 1904.)

Taking No. 5 of the above table of analyses we find that it contains 87.96 per cent of clay substance. This point is plotted in the first column. The point representing the percentage of fine silt is then plotted in the next column, and so on with the other sizes. These points are then connected with a curved line. In the same way the percentages of the different sizes of grains of the other samples were plotted and connected by curved lines. The lines are drawn in different ways, so that those representing the different clays can be more readily distinguished at a glance. From a study of this table it is seen that the clay having the lowest tensile strength (No. 5) contains a very high percentage of the finest clay particles, furthermore, the clay having the second lowest tensile strength (No. 4) contains the largest percentage of sand (42.9 per cent). From this it appears that an excess of either coarse or fine grains lowers the tensile strength. On the other hand, in those clays having the highest tensile strength the percentages of fine, medium, and coarse particles are more nearly equal. This is perhaps what might be expected, for if the tensile strength is due to the interlocking of the grains, a mixture of different sizes would fit together more closely than if particles of one size predominated, as in Nos. 4 and 5 of the table. It is rather difficult, however, to compare these results with Orton's, as in his artificial mixtures the non-plastic particles were of uniform size, while in the natural mixtures a variety of sizes existed.

Beyer and Williams[1] reached somewhat similar conclusions at about the same time, their work on the mechanical analyses of the loess-clays indicating that the clays showing the highest tensile strength were the ones in which there was the most evenly proportioned amounts of the sizes of the grains represented, therefore those possessing a large proportion of excessively fine particles or those running high in some intermediate size of grain are weaker. The following mechanical analyses made by them indicate this:

MECHANICAL ANALYSES OF IOWA LOESS CLAYS

Clay	Loss at 230°	Size of clay particles					Total per cent	Average tensile strength, pounds
		Above .1 mm.	.1 to .05 mm. incl.	.05 to .01 mm. incl.	.01 to .003 mm. incl.	Below .003 mm.		
Besley, Council Bluffs, top clay	1.55	3.44	22.10	49.11	13.44	10.35	99.99	149
Gethman, Gladbrook	2.59	5.19	22.46	32.04	14.15	23.55	99.98	279
Besley, Council Bluffs, bottom clay	2.04	1.62	25.26	29.72	17.85	23.74	100.23	244

If the theory of interlockment is true, then it should be possible to make a mixture of two clays whose tensile strength is higher than that of either of the clays alone or vice versa.

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[1] Ia. Geol. Surv., Vol. XIV, p. 102, 1904.

The writer [1] has noted a case of two clays from near Asbury Park, N. J. One of these was a slightly gritty, black clay, with an average tensile strength of 182 lbs. per square inch. The other was a plastic loam, whose average tensile strength was 137 lbs. per square inch. A mixture of the two in equal proportions, however, had an average tensile strength of 258 lbs. per square inch.

Another clay from a different formation had an average tensile strength of 108 lbs. per square inch, while a mixture of equal parts of this clay and a somewhat coarse sand had a tensile strength of but 65 lbs. per square in., the decrease being evidently due to the excess of sand.

Grimsley and Grout claimed that a constant relation exists between the tensile strength of a clay and the percentage of soluble salts which it contains.[2] While it is true that each series, when plotted by itself, shows a parallel rise between salts and tensile strength, yet no such regularly ascending curve would be obtained if all the data were combined into one. For example, the amount of soluble salts (0.40) in the West Virginia clays of 150 lbs. tensile strength, is hardly any greater than those of the New York series (0.37) ranging from 0–50 lbs. in tensile strength.

COMPRESSIVE STRENGTH

The compressive strength of unfired clay is rarely determined and comparatively few tests have been published.

Scattered data give the compressive strength of dried washed kaolin from 200–400 lbs. per sq. in., and of ball-clays from 400–1200 lbs. per sq. in.

Range of compressive strength.—The following figures from Bleininger and Howat,[3] give crushing strength of the dried clay alone, and

COMPARATIVE STRENGTH TESTS OF CLAY WITH AND WITHOUT SAND

	Without sand			With sand		
	Compression	Tensile	Transverse	Compression	Tensile	Transverse
Ball clays........	565–1148	135–210	375–558	464–777	124–180	242–330
Plastic clays......	631–954	155–172	484–520	476–553	113–150	216–280
Shales...........	636–806	126–187	311–403	403–449	77–111	178–237
Plastic kaolins....	455–539	104–147	239–325	286–559	54–110	122–210
Primary kaolins...	205–349	34– 69	74–166	164–172	29– 35	56– 82

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[1] N. J. Geol. Surv., Final Report, Vol. VI, p. 90, 1904.

[2] W. Va. Geol. Surv., III, p. 58, 1906.

[3] Trans. Amer. Ceram. Soc., XIV, p. 274, 1914. See also Schurecht, U. S. Bur. Stand., Bull. 79, 1916.

when mixed 1 : 1 with standard Ottawa sand, as well as the tensile and transverse tests.

STRENGTH OF FIRED CLAYS

The following tests, by Schurecht, of the transverse strength on dried and fired clays,[1] indicated that while the modulus of rupture is considerably higher in the fired than in the green state, it does not appear to increase steadily with the temperature of burning.

It was found that with one exception they developed their maximum strength at cone 8, even though porosity and shrinkage data indicated them to be under- or over-fired at this temperature. The cause of weakening above cone 8 was thought to be due to the formation of "sillimanite."

TRANSVERSE STRENGTH OF DRIED AND FIRED CLAYS

		Modulus of rupture, pounds, square inches, dried, 110° C.	Modulus of rupture of burned clay		
			Cone 6	Cone 8	Cone 10
Tionesta clay, Ellis, Muskingum Co., O.	1.	389.5	4,624	6680	3812
	2.	467.9	7,200	8265	5330
Lower Kittaning clay, unweathered, Roseville, Muskingum Co., O.	1.	218.6	3,190	3416	2665
	2.	319.5	8,556	8680	7504
Lower Mercer clay, White Cottage, Muskingum Co., O.	1.	132.0	2,964	3223	1670
	2.	250.7	5,703	7285	4681
Mogodore, Summit Co., O.	1.	142.5	2,023	2283	2181
	2.	259.0	4,666	4820	3361
Lower Kittanning clay, Fire-brick, Lawrence Co., O.	1.	324.9	4,068	5075	3014
	2.	499.2	10,448	7190	6175

1. = Run of mine, ground to pass 20 mesh.
2. = Washed clay, passing 150 mesh sieve.

A similar strength peak was noted by Ries and Oinouye [2] in testing the tensile strength of some fired clays (Fig. 63).

Another series of experiments,[3] made on mixtures of seven different fire-clays with grog (burned to cone 15 and ground to pass 10 mesh), showed that repeated heating decreased the strength, but each mixture showed a slight increase at some point beyond which the strength again decreased.

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[1] Schurecht, U. S. Bur. Stand., Tech. Pap. 233, p. 33, 1920; also Jour. Amer. Ceram. Soc., IV, p. 366, 1921.

[2] Trans. Amer. Inst. Min. Engrs., LVIII, p. 184, 1918.

[3] Kirkpatrick, F. A., Trans. Amer. Ceram. Soc., XVIII, p. 545, 1916.

Bleininger[1] in a study of the relation between the porosity and crushing strength of clay products noted that the compressive strength seems to increase rapidly as porosity is decreased below 3-4 per cent, and less rapidly as it is decreased to this value.

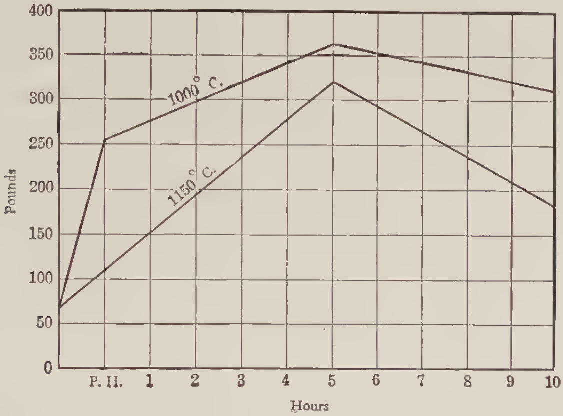

Fig. 63.—Tensile strength of a clay air dried, and after firing. Ries and Oinouye, Trans. Amer. Inst. Min. Engrs., LVIII, 1918.

Plastic Strength

In this test described by R. F. MacMichael,[2] the plastic briquette is held in wooden clips, standard Ottawa sand flows through a small opening from the container into a bucket suspended from the lower wooden clip. When the flow of sand is less than 2 lbs. per minute, the comparative results are not as uniform as when the rate of application of the load is greater. Wilson states that in general the plastic tensile strength indicates the plasticity of clays, but that individual comparisons are often misleading.[3] Figure 64 shows some results obtained with this test.

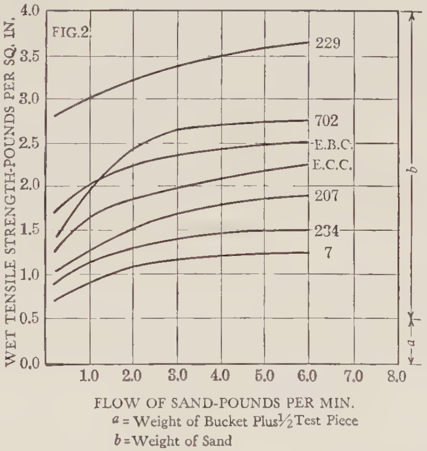

Fig. 64.—Curves showing plastic tensile strength of several clays. (After Wilson, Univ. Wash., Eng. Exp. Sta., Bull. 18, 1923.)

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[1] Trans. Amer. Ceram. Soc., XII, p. 564, 1910.

[2] Trans. Amer. Ceram. Soc., XVII, p. 639, 1915.

[3] Wilson, H., Univ. Wash., Bull. Eng. Exper. Sta., No. 18, 1923.

SHRINKAGE

All clays shrink in drying and burning, the former loss being termed the air-shrinkage and the latter the fire-shrinkage.

Air-shrinkage.—In clay which is perfectly dry all the grains are in contact, but between them there will be a variable amount of pore-space depending on the texture of the clay. The volume of this pore-space is indicated somewhat by the quantity of water that will be absorbed without the clay changing its volume, this water filling in the space between the grains. It may be termed pore water.

The presence of more water than is required to fill the spaces between the grains produces a swelling of the mass, and in this condition each grain is regarded as being surrounded by a film of water; but while the grains still mutually attract each other the attraction is less than in the dry clay, and the mass yields readily to pressure. An excess, however, separates the clay particles to such an extent that the clay softens and runs. A clay will therefore continue to swell as water is added to it, until the amount becomes too great to permit it to retain its shape.

Some clays absorb very little water, while others take up a large quantity, and G. P. Merrill[1] mentions one from Wyoming which when placed in a measuring-flask absorbed and retained sufficient water to increase its bulk eightfold.

When a clay has been mixed with water and set aside to dry evaporation of the moisture commences and the particles of clay draw closer together, causing a shrinkage of the mass. This will continue until all the particles come in contact, but since they do not fit together perfectly there will still be some pore-spaces left between the grains, and these will hold moisture which cannot be driven off except by heating at 105° C. The air-shrinkage may therefore cease before all the water has passed off.

The amount of water added to a clay may have considerable effect on its drying shrinkage, but according to some exerts comparatively little effect on the physical properties of the burned mass, although the latter point is disputed by others.[2]

The rate of evaporation of the water from the clay will naturally be governed by the capillary flow of moisture from the interior of the mass towards the surface. In highly colloidal clays therefore the water will evaporate at a more rapid rate from the surface, than it can be supplied from the interior, so that stresses are developed which may cause visible or invisible cracking.[1]

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[1] The Non-metallic Minerals, p. 233.

[2] Montgomery, R. J., and Fulton, C. E., Trans. Amer. Ceram. Soc., XVII, p. 437, 1915.

According to Bleininger the permeability of the clay to water may be said to vary as $K\ r^3$, where K = a constant, and r = mean radius of the particles.

While different clays, differ greatly in their amount of air-shrinkage and rapidity with which they can be dried, it appears that the total shrinkage depends on the water content, and is not influenced by the rapidity of drying. The drying time depends on the water content and also the structure of the clay.[2]

The air-shrinkage, in addition to varying with amount of water used for tempering, will also range with the size and shape of the piece.

To obtain more uniform results, it is safer to take the dry volume or dry length as the basis of measurement.

Even this may not give uniform results, because the dry volume may vary with the drying treatment.

For greatest accuracy the true volume of the dry-clay grains may be used as the basis for shrinkage measurements, but this involves true specific gravity determinations, etc.

If the linear shrinkage of a test piece is measured, it will be found to vary in different directions, and for this reason it may be more desirable to give the volume air-shrinkage of the clay.

Sand or materials of a sandy nature counteract the shrinkage, and are frequently added for this purpose, but, since they also render the mixture more porous, they facilitate the drying as well, permitting the water to escape more readily, and reducing the danger from cracking. If the sand added to dilute the shrinkage is refractory it also aids the clay in retaining its shape during burning.

The effect of sand on a clay is well seen from the following experiment with a clay from Herbertsville, N. J.:

	I	II	III
Clay..................	32.6	5.3	108
Clay + 50 per cent sand.	15.6	3.3	65

I. Per cent of water required.
II. Per cent of air-shrinkage.
III. Tensile strength, pounds per square inch.

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[1] Bleininger, A. V., Colloid Symposium Monograph, II, p. 90.

[2] Geller, R. F., Jour. Amer. Ceram. Soc., IV, p. 282, 1921.

From the above it is seen that the addition of 50 per cent of sharp sand reduced the amount of water required a little over one-half. The air-shrinkage was reduced 37.73 per cent, but it was accompanied by a loss in the tensile strength of nearly 40 per cent.

Expression of air-shrinkage.—The air-shrinkage of a clay may be expressed either in terms of its length (linear air-shrinkage) or in terms of its volume (volume air-shrinkage).

To determine the linear air-shrinkage, a straight line is ruled on the test bricklet, with two cross lines, a definite distance apart.

After the clay has been first air-dried, and then at 105° C. in a hot-air bath, the distance between the two cross lines is measured and from this the linear air-shrinkage computed in terms of the wet length, or if desired in terms of the dry length.

To determine the volume shrinkage, the freshly molded test piece is placed in a volumeter (see Volumeters) filled with kerosene, and its volume determined. The bricklet is then thoroughly dried, soaked for twelve hours in kerosene of the same specific gravity as that used in the volumeter, and its volume again determined.

The volume can be determined from the formula:

$$\frac{V_1 - V_2}{V_1} \times 100 = \text{volume shrinkage},$$

in which V_1 = wet volume;

V_2 = dry volume.

The linear air-shrinkage may be calculated from the volume shrinkage by the following formula:

$$a = \left(1 - \sqrt[3]{\frac{1-b}{100}}\right) \times 100,$$

in which a = per cent linear shrinkage;

b = per cent volume shrinkage.

Range of air-shrinkage.—The following figures give the range of linear and volume air-shrinkage of several classes of clays, collected from a number of different sources:

Linear and Volume Air Shrinkage of Different Clays

	I	II
Crude kaolin	5.0 – 7.60	14.11–20.92
Washed kaolin	3.3 –10.80	20.20–28.91
White sedimentary kaolin	4.5 –12.50	7.53–36.46
Ball clay	5.25–12.0	21.9 –31.92
Crucible clay	6.7 –15.0	18.98–55.05
Refractory band clay	4.25–11.0	30.48–45.00
Glass pot clay	3.31– 9.5	20.57–48.80
Plastic fire clays	1.7 – 9.4	6.67–28.80
Flint fire clays	0.78– 6.59	2.36–21.12
Sagger clays	2.8 –10.8	9.10–25.0
Stoneware clay	4.8 – 9.3	15.11–41.2
Face brick clay	2.4 – 5.66	7.60–17.95
Sewer pipe clay	3.5 –10.5	16.12–22.9
Paving brick clay	0.9 – 5.82	3.54–18.29

I. Per cent of linear air-shrinkage.
II. Per cent of volume air-shrinkage.

Effect of pressure on air-shrinkage.—The amount of pressure applied to a wet clay, seems to have little or no effect on the air- and fire-shrinkage of a clay or its porosity after firing. The following figures, by C. W. Parmelee,[1] show the amount of moisture in the clay after compression, and porosity after firing at cone 6½:

Effect of Pressure on Porosity and Moisture Content

Pounds of pressure on whole surface	Moisture content, per cent	Apparent porosity, per cent *	Total porosity, per cent †	Open pores, per cent †	Sealed pores, per cent †
Molded by hand	18.40	20.47	33.35	27.29	6.06
2,000	17.00	20.67	32.94	27.49	5.45
8,000	17.00	20.73	32.10	27.38	4.72
15,000	17.20	20.46	31.40	26.82	4.85
30,000	16.90	20.71	32.13	27.37	4.76
50,000	15.60	21.44	33.30	28.58	4.82

* Calculated in terms of whole volume.
† Calculated in terms of volume of the solid.

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[1] Trans. Amer. Ceram. Soc., XVI, p. 195, 1914.

Bailey [1] argues that because the air shrinkage varies with the method of preparing the test pieces, that it is of little value as compared with the volume shrinkage. It is not quite clear, however, why the latter would not be affected by the same factors.

Preheating.—It has been noticed that in some highly plastic clays the air-shrinkage may be reduced by preheating them to temperatures up to 500° C.[2] This treatment produced a notable decrease in the shrinkage but the effect was much less in clays of moderate or low plasticity. The reason for the change is to be assigned to the destruction of some of the colloidal matter.

As examples: Tennessee ball clay No. 3 had a volume air shrinkage of 42%. After preheating to 350° C it was 22%, and after 450° C it was 8 per cent.

A very sticky surface clay with a volume shrinkage of 44 per cent, showed 12 per cent after heating to 350° C., and 9 per cent after 450° C.

Factors affecting air-drying.—The speed with which it is safe to air dry clays, varies with the character of the material. Open, porous or sandy clays are usually easier to dry than dense, highly plastic ones, for in the latter the water is evaporated more rapidly from the surface, than it can be drawn from the interior. The result is the development of stresses which may cause cracking.[3]

The time of drying is naturally an important element, and very plastic clays may require slower drying than less plastic ones.[4]

Some idea of the drying qualities of a clay may be obtained from tests made with small samples, insofar as they serve to separate the very bad from the good drying clays. There may be an intermediate class which give good results with small test pieces, but do not dry well in large ones.[5]

According to Wilson, " the drying ability of large-size pieces of clay ware cannot be accurately expressed in numerical terms of strength, shrinkage, time of drying, etc."

The factors aiding safe drying are: (1) Pore space of body, (2) plastic strength, (3) dry strength. The factors indicating resistance to drying are: (1) Shrinkage, and (2) time of drying.

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[1] Trans. Amer. Ceram. Soc., XVIII, p. 557, 1916.

[2] Brown and Montgomery, U. S. Bur. Stand., Tech. Pap. 21; see also Orton, E., Jr., Trans. Amer. Ceram. Soc., XIII, p. 765, 1911; Keele, J., ibid., XIV, p. 152, 1912.

[3] See also Lindsay, D. C., and Wadleigh, W. H., Jour. Amer. Ceram. Soc., VIII, p. 677, 1925.

[4] See R. P. Geller, Jour. Amer. Ceram. Soc., IV, p. 282, 1921.

[5] Wilson, H., Bull. Univ. Wash. Eng. Exper. Sta., No. 18, 1923.

These factors expressed numerically can be combined in the following equation:[1]

$$\text{Safety of drying} = \frac{(\text{per cent pore water}) \times (\text{plastic tensile strength} \times (\text{dry transverse strength})}{(\text{per cent volume shrinkage}) \times (\text{time of drying})}$$

Bleininger[2] suggests using the formula: Resistance of clay to drying = (per cent linear shrinkage) × (time in hours for complete shrinkage).

The time in hours for complete shrinkage is ascertained by repeated measurements of the linear dimensions, when a given sized test piece is subjected to constant temperature (63°) and humidity conditions.

Repeated volume measurements can also be made and are considered more reliable.

Fine-grained clays often crack badly in drying.

Casselman drying test.—A laboratory method to determine the drying characteristics of clays has been suggested by E. J. Casselman[3] as follows:

" (1) Grind the clay to pass a 40-mesh screen; (2) take three samples of the ground clay, approximately 25 grams each, designated as A, B, and C; (3) blunge samples A and B[4] with just sufficient water to make a slip that will barely flow, and allow to stand for thirty minutes; (4) blunge sample C with enough water[5] to make it flow very freely, and ' age ' for half an hour before pouring; (5) pour the three samples upon the smooth surface of a plaster slab;[6] (6) smooth over and flatten with the finger samples A and B to avoid drying in a conical shape; (7) when the water of the sample A has been removed by the plaster to the extent that the upper surface is no longer wet or adherent to a spatula, remove the sample from the plaster and make into a suitable form for determination of drying shrinkage. A cube is satisfactory; (8) leave samples B and C on the plaster slab without being touched until they are dry; (9) allow all the samples to dry naturally in the air.

" The following observations are made on the different test-pieces when dry: (1) Drying shrinkage is determined upon test-piece A, either by volume or length, but if the former, the linear shrinkage should be computed from it. (2) It will be found in the drying of the test-piece B that the surface against the perfectly smooth plaster is in a slightly warped condition of a convex character. This surface may be irregular and frequently has a varying radius of curvature at different points. The measurement that is made is the average radius of curvature of this surface at the edge of the test-piece. One method of making this measurement is to tip the test-piece up on edge by pressure with the fingers, so that the plaster base is tangent to the large surface at its junction with the boundary edge. The diameter of the test-piece and the distance the opposite edge is raised from the plaster are measured as shown in Fig. 65. The radius of curvature is computed from the formula

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[1] Wilson, H., Univ. Wash. Eng. Exper. Sta., Bull. 18, p. 31, 1923.

[2] U. S. Bur. Stand., Tech. Pap. 79, p. 20.

[3] Jour. Amer. Ceram. Soc., X, p. 59, 1927.

[4] The blunging is done in a porcelain mortar with an egg beater.

[5] At least 2.5 cc. of water should be used for every gram of clay.

[6] The diameters of the wet pieces, A and B should be 7 to 8 cm.

$$R = \frac{D^2}{2H'}$$

wherein D is the diameter of the specimen, H^1 is the height of the raised edge, and R is the radius of curvature. The measurement should be made at several points around the test-piece, so that a fair value for the average radius can be computed. (3) The amount of cracking in test-piece C is observed. These test-pieces generally show either a few large cracks that begin at the edge of the test-piece and extend inward, or else a large number of cracks that check the entire body of the testpiece. Interpretation: (1) Clays with good drying properties have (*a*) low drying shrinkage, 7 per cent or less, on the test-piece A; (*b*) a large radius of curvature, 40 cm., or more, in test-piece B; (*c*) a small amount of cracking, less than five major cracks, in test-piece C. (2) Clays with poor drying properties have: (*a*) a high drying shrinkage, 10 per cent, or more, on test-piece A; (*b*) a short radius of curvature, 20 cm., or less, on test-piece B; (*c*) a large amount of cracking and checking on test-piece C. (3) Clays with intermediate drying properties have various combinations of these properties."

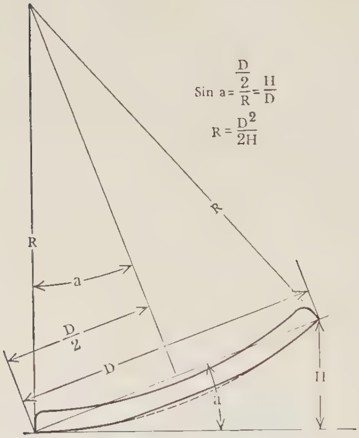

Fig. 65.—Method of measuring the radius of curvature of test piece B. (Casselman, Jour. Amer. Ceram. Soc., X, 1927.)

Fire-shrinkage.—All clays shrink during some stage of the firing, even though they may expand slightly at certain temperatures. The fire-shrinkage, like the air-shrinkage, varies within wide limits, the amount depending partly on the quantity of volatile elements, such as combined water, organic matter, and carbon dioxide, and partly on the texture and fusibility.

Fire-shrinkage may begin at a dull-red heat, or about the point at which chemically combined water begins to pass off and reaches its maximum when the clay vitrifies, but does not increase uniformly up to that point. The clay worker, however, always tries to get a low fire-shrinkage, using a mixture of clays if necessary in order to prevent cracking and warping. After the expulsion of the volatile elements the clay is left in a porous condition, until the fire-shrinkage recommences. In the table[1] following there are given the results of a series of tests made on eight different clays, which were burned at temperatures 100° C. apart from 500° C. up to 1100° C. inclusive.[2]

TABLE SHOWING PROGRESSIVE SHRINKAGE AND LOSS OF WEIGHT AT DIFFERENT TEMPERATURES

Laboratory number	Per cent of air-shrinkage	Per cent of weight lost in air-bath	500° C. 932° F.	600° C. 1112° F.		700° C. 1292° F.		800° C. 1472° F.		900° C. 1652° F.		1000° C. 1832° F.		1100° C. 2012° F.	
			Per cent of weight lost	Per cent of weight lost	Per cent of fire-shrinkage	Per cent of weight lost	Per cent of fire-shrinkage	Per cent of weight lost	Per cent of fire-shrinkage	Per cent of weight lost	Per cent of fire-shrinkage	Per cent of weight lost	Per cent of fire-shrinkage	Per cent of weight lost	Per cent of fire-shrinkage
648	9.0	2.69	6.38	1.72	0.3	0.70	0.0	0.88	0	0.56	0	0.19	0.7	0.38	4.0
655	4.6	1.36	6.10	1.38	0.0	0.55	0.0	0.33	0	0.33	0	0.12	0.7	0.21	2.4
663	5.3	1.50	4.24	1.37	0.7	0.35	0.3	0.05	0	0.27	0	+0.06	0.0	0.19	1.3
665	7.0	1.43	8.65	1.07	0.3	0.48	0.0	0.39	0	0.12	0	0.10	2.7	0.00	12.6
696	5.6	3.48	9.42	2.61	0.4	1.61	0.0	0.46	0	0.33	0	0.14	1.3	0.22	4.7
703	1.0	0.63	2.52	1.05	0.0	0.26	0.0	0.10	0	0.02	0	0.09	1.4	0.03	0.0
717	8.0	3.29	5.32	1.70	0.3	0.83	0.0	0.41	0	0.49	0	0.34	1.3	0.24	4.0
728	2.0	0.70	3.23	1.03	0.6	0.61	0.0	0.22	0	0.15	0	0.10	1.3	0.12	2.7

Explanation of table.—The clays tested were the following:

648. Fat, black, micaceous clay, of Clay Marl I from Maple Shade, N. J.

655. A clay marl. Exact locality unknown.

663. A Pleistocene clay from Vineland, N. J.

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[1] N. J. Geol. Surv., Fin. Rept., Vol. VI, p. 92, 1904.

[2] Ibid., p. 94, 1904.

665. A yellow, finely gritty, Cohansey clay, heavily stained with limonite from Toms River, N. J.

696. Black, Asbury clay from west of Asbury Park, N. J.

703. Sandy, Raritan clay from near Fish House, N. J.

717. A very plastic clay from Clay Marl III, south of Woodbury, N. J.

728. Hudson River shale from Port Murray, N. J.

The bricklets had been standing in a warm room for several weeks, and, although they appeared perfectly dry, they were placed in a hot-air bath and kept at a temperature of 110° C. for a day, being weighed both before and after. This drove off the moisture remaining in the pores, and the resulting loss in weight indicated in the third column of the above table shows the quantity of moisture that may remain in a brick after the air-shrinkage has ceased. It is least in the sandy, lean clays and highest in the black one, which is colored by organic matter. The second column indicates the per cent of air-shrinkage, calculated upon the length of a freshly molded bricklet. The fourth column, headed 500° C. gives the loss in weight from the thoroughly dried condition (at 105° C.) up to 500° C., calculated on the weight of the air-dried sample. The following columns give the additional loss in weight for each 100° C., as well as the fire-shrinkage taking place in this temperature interval. From an inspection of the table it is seen that most of the volatile substances, such as the chemically combined water contained in the hydrous aluminum silicate, mica, or limonite, and organic matter, pass off before 500° C., and that an additional appreciable amount is expelled between 500° C. and 600° C. Between 600° C. and 1100° C. there was a small but steady loss, while in one case (No. 663) there was even a gain in weight at 1000° C. Two samples, Nos. 696 and 665, showed a high loss at 500° C. and 600° C., as compared with the others, but this was due to the former containing considerable organic matter, and the latter having a very high percentage of limonite, which would supply an additional quantity of chemically combined water.

The amount of fire-shrinkage shown by these samples is equally interesting, for it is seen that, although the loss in weight between 500° C. and 900° C. is considerable, still there is little or even no shrinkage, so that, after the volatile elements have been driven off, the clay must be very porous, and remains so until the fire-shrinkage begins again. From the table it will be seen that, with one exception, no shrinkage occurred between 600° C. and 900° C.; but between 900° C. and 1000° C., all except No. 663 decreased in size, and there was an additional but greater shrinkage between 1000° C. and 1100° C. None of the bricklets became steel-hard, that is, sufficiently hard to resist scratching with a knife, until 1000° C., or even 1100° C. In the case of those burning red, a good red coloration began to appear at 1000° C. From this it can be seen, and this is a fact already known, that, up to 600° C., a clay should be heated slowly; but from that point up to 1000° C. the temperature can be raised quite rapidly, unless much carbonaceous matter is present. The gradual burning-off of this carbon is well shown in Fig. 45, which represents a series of bricks taken from a kiln at regular intervals as the burning proceeded. Further heating should be done slowly, as the shrinkage recommences at the last-mentioned temperature.

Some clays may expand slightly at low temperatures. In one series of British fire-clays tested[1] it was found that in most of them there was one temperature below 900° C. at which sudden expansion occurs. These changes it is pointed out are most likely to be connected with allotropic changes in the quartz present.

A kaolin heated very slowly to 1080°[2] showed a slight expansion up to 530° C., at which temperature a marked contraction started, and continued for two days, while the temperature was maintained constant. Another pronounced contraction took place between 680°–710° C., and again at 870° and 950°, after which there was no further shrinkage up to 1080° C. These changes were apparently not due to vitrification.

Some highly calcareous clays expand slightly in the early stages of firing.

While the fire-shrinkage may be due mainly to the progress of vitrification (see Vitrification), there are undoubtedly other causes, which operate particularly at lower temperatures, for, as pointed out by Bleininger and Brown,[3] a shrinkage takes place above the temperature of dehydration, which is analogous to the shrinkage of alumina, magnesia, and other typically amorphous bodies. Since this may be shown markedly by some very pure clays, it cannot represent contraction caused by vitrification.

Kaolin begins to contract soon after the chemically combined water is driven off, when the substance is a typical amorphous body. A flint clay is cited whose contraction practically ceased at cone 1, and remained constant in volume for a long temperature interval up to cone 22.

The fire-shrinkage varies widely in different clays, and may proceed at very different rates (see Vitrification).

Since many clays, when used alone, shrink to such an extent as to cause much loss from warping and cracking, it is necessary to add materials which of themselves have no fire-shrinkage, and so decrease the shrinkage of the mixture in burning. Sand or sandy clays are the materials most commonly used for this purpose, but ground bricks

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[1] Firth, Hodkin and Turner, Jour. Soc. Glass. Technol., IV, p. 163, 1920.

[2] Houldsworth and Cobb, Trans. Ceram. Soc. (Eng.), XXII, p. 111–137.

[3] U. S. Bur. Stand., Bull. 7, p. 22.

(grog), may be employed. They furthermore add to the porosity of the ware, and thus facilitate the escape of the moisture in drying and in the early stages of burning, as well as enabling the product to withstand sudden changes of temperature. If sand is added for this purpose, it may act as a flux at high temperatures, and this action will be the more intense the finer its grain.

Large particles of grog are undesirable, especially if they are angular in form, because, in burning, the clay shrinks around them, and the sharp edges, serving as a wedge, open cracks in the clay, which may expand to an injurious degree. Large pebbles will do the same, and at many common brickyards it is not uncommon to see bricks split open during the burning, because of some large quartz-pebble left in the clay, as the result of improper screening of the tempering sand. For common brick, the type of sand used does not make much difference, as long as it is clean; but if sand is to be added to fire-brick mixtures, it should be coarse, clean, quartz-sand. Burned clay-grog is more desirable than sand for high-grade wares, since it does not affect the fusibility of the clay, or swell with an increase of temperature as sand does, but precaution should be taken to burn the clay to its limit of shrinkage before using it.

Measurement of fire-shrinkage.—Either the linear or volume fire-shrinkage may be determined, and in the same manner as explained under air-shrinkage, except that in addition the temperature or cone (see Seger Cones) at which the shrinkage is determined should also be given.

The shrinkage may be expressed in terms of the volume or length as moulded, or in that of the dried clay.

The formula for volume fire-shrinage expressed in terms of the dry clay would be:

$$\text{Volume shrinkage} = \frac{(V_1 - V_2)100}{V_2};$$

V_1 = volume of dry clay;

V_2 = volume of burned clay.

A method for measuring the fire-shrinkage suggested by W. C. Broga and C. J. Hudson[1] consists in measuring the circumference of clay discs by means of a wire stretched around the outside. It can be graduated to read the circumference of the discs in centimeters, or if they are all of the same initial size it can be calibrated to read the percentage shrinkage directly.

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[1] Jour. Amer. Ceram. Soc., V, p. 34, 1922.

CHAPTER V

PHYSICAL PROPERTIES OF CLAY *(continued)*

DETERMINATION OF VOLUME

THE determination of the volume of either raw or fired clay may be necessary for measuring volume shrinkage during drying or firing. Several different types of apparatus have been designed for this purpose.

In most of them the test piece has to be soaked in water or kerosene, in order to fill the pores, before it is placed in a corresponding liquid in the volumeter. This is avoided in the type of volumeter using mercury as the immersing medium.

Several different forms are described below:

Seger volumeter. — This consists (Fig. 66) of a four-litre, wide-mouthed, glass-stoppered jar. A circular opening in the center of the stopper is fitted with the ground-end of a short glass tube *m*, which expands above into a bulb *b*, and is again contracted above it. The jar has a glass stopcock *e* near its base, which is connected above with a burette *a* of 125 c.c. capacity, and graduated to tenths. The upper end of the burette also widens to a bulb *f*, from the top of which there extends a bent tube for the attachment of a rubber, this tube being used to draw the liquid into the burette.

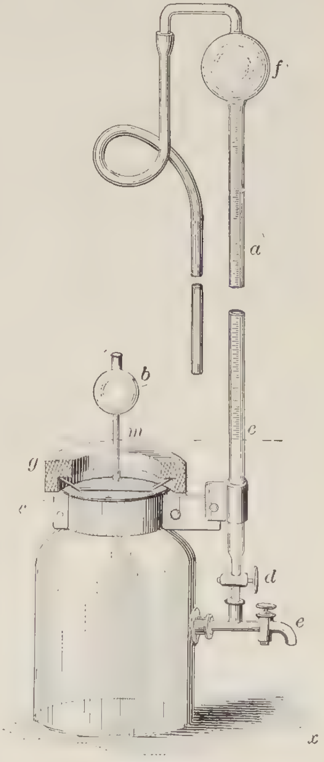

FIG. 66.—Seger's volumeter, for determining porosity and volume.

When the stopcock in the lower part of the burette is open, and the liquid filled in jar up to the mark on the small glass tube *m*, the liquid stands at the zero-point in the burette.

The method of using the apparatus, together with the results obtained on a number of Iowa clays, was as follows:[1]

To use the volumeter for determining the volume of clay, it is filled with oil, ordinary kerosene with a specific gravity of 0.8 (which must be accurately known) having been found to give satisfactory results.

After filling the jar the burette is drawn full of the liquid by suction through the rubber tube, and held full by turning the burette-valve or by means of a pinch-cock on the rubber. The stopper is now removed and the test-piece of the clay put in. The stopper is now replaced, and by releasing the pinch-cock *d*, oil from the burette is allowed to flow back into the jar until it stands at the mark on the short tube.

The volume of the clay is then indicated by the height of the liquid in the burette above the zero mark. The piece of clay is taken out and placed to dry while the volumeter is again filled to the zero points to be ready for the next test.

When dry the clay is heated to 105° C. to expel all hygroscopic moisture and after weighing it is placed in a vessel of oil until saturated. When saturated the volume of the piece is measured as before. Having now the wet and dry volumes, the percentages of cubical shrinkage in drying are easily calculated.

A serious objection to the Seger volumeter is its cumbersome character and the time required for operation.

Pycnometer volumeters.—A type described by Schurecht[2] is that illustrated in Fig. 67, which is made of glass. To operate the bottle is filled with kerosene or water, and as stopper is inserted sufficient liquid is forced into the tube in stopper to fill it completely. The excess liquid is wiped off and bottle weighed. The briquette to be measured is then placed in bottle and operation repeated.

The calculation is:

$$V = \frac{W - W_1 + B}{S}$$

V = Volume;

W = Weight of bottle plus liquid;

W_1 = Weight of bottle plus liquid plus briquette;

B = Weight of saturated briquette;

S = Specific gravity of liquid.

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[1] Ia. Geol. Surv., Vol. XIV, p. 107, 1904.

[2] Jour. Amer. Ceram. Soc., I, p. 556, 1918.

Precautions: Weight of bottle plus liquid should be checked at intervals. A scratch on side of bottle is used to insure stopper being placed each time in same position.

Shaw's volumeter[1] is shown in Fig. 68. The procedure is given as follows: 1. Saturate the briquette with liquid (kerosene, if green; water, if burned). 2. Place briquette in volumeter. 3. Fill volumeter to mark. 4. Remove stopper and briquette. 5. Replace stopper in same position as original. 6. Run liquid from burette through the tube in stopper until the bottle is filled to the mark. 7. Read the volume directly from burette. The experimental error in manipulating this apparatus will approximate about 0.1 c.c.

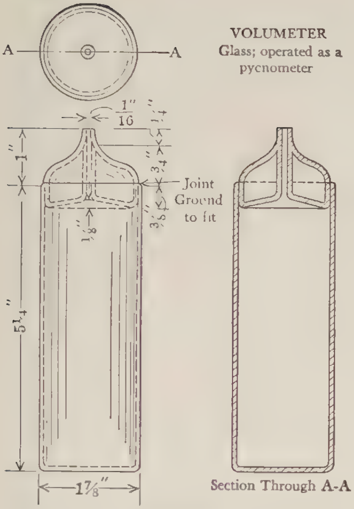

Fig. 67.—Pycnometer volumeter of Schurecht. (Jour. Amer. Ceram. Soc., I, p. 918.)

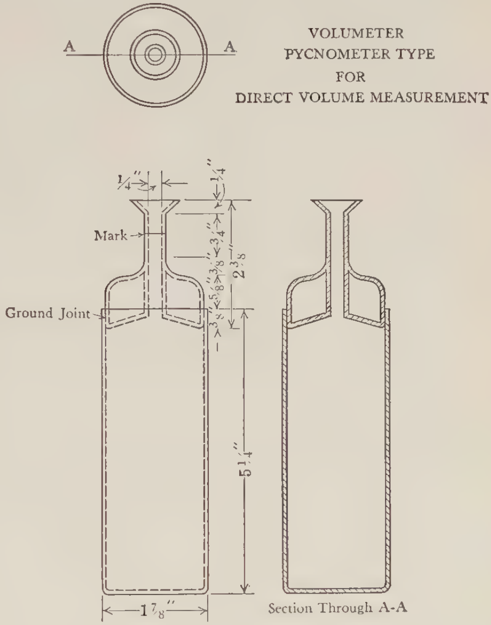

Fig. 68.—Shaw's volumeter of pycnometer type. (Jour. Amer. Ceram. Soc., II, 1919.)

Direct-reading overflow volumeter.—A direct-reading overflow volumeter designed by the Ceramic Experiment Station of the Bureau of Mines[2] is shown in Fig. 69. It consists of a glass cylinder 4.75 cm. diameter and 16.26 cm. high. An overflow tube passing through the bottom, extends 10.25 cm. upward inside the cylinder. Under the cylinder is placed a special burette graduated with reverse reading to measure the overflow from cylinder. A brass spoon for immersing the test-piece is suspended by means of a hook from the top of the cylinder, and extends to $\frac{1}{8}$ inch from the bottom.

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[1] Jour. Amer. Ceram. Soc., II, p. 481, 1919.

[2] Schurecht, H. G., Jour. Amer. Ceram. Soc., III, p. 731, 1920.

To operate, the cylinder is filled with liquid (water or kerosene) to level of overflow. The spoon is then removed and after placing test-piece on it, it is lowered into cylinder. This causes the liquid to overflow, until its level drops to that of the overflow opening. The volume of liquid which runs into the burette is noted and this gives the volume of the test-piece. The method is rapid and accurate.

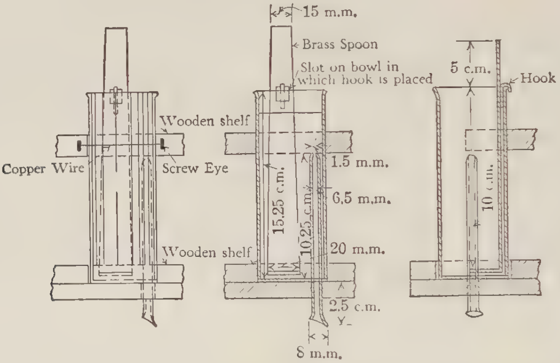

FIG. 69.—Direct reading overflow volumeter. (Schurecht, Jour. Amer. Ceram. Soc., III, 1920.)

Crawford method.—The following method has been suggested by Crawford [3] to obviate the necessity of soaking in kerosene.

Some extra briquettes are made, weighed dry and saturated with kerosene. Their bulk specific gravity may be determined by one of the following methods:

$$\text{Bulk sp. gr.} = \frac{\text{Dry weight}}{\text{Volume}} \text{ (By volumeter).}$$

$$\text{Bulk sp. gr.} = \frac{\text{Dry weight} \times \text{sp. gr. kerosene}}{\text{Saturated weight} - \text{suspended weight}} \text{ (Weighing method.)}$$

The bulk specific gravity figure obtained as above is then used in the formula given below, for determining the volume of additional dried bricklets of the same clay, or even of fired samples.

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[3] Jour. Amer. Ceram. Soc., V, p. 394, 1922.

$$\text{Volume} = \frac{\text{Dry weight}}{\text{Bulk specific gravity}}.$$

The particular advantage is that it reduces weighings and obviates necessity of soaking in kerosene and then evaporating the latter.[1]

Mercury volumeter.—This instrument is of somewhat[2] different type from others used in that mercury instead of kerosene or water are used. The apparatus (Fig. 70) consists of a "burette which may be lowered by means of a rack and pinion. To the lower end of the burette there is a rubber tube attached which connects at the other end with the reservoir. This reservoir is at a fixed point, level with the bottom of the burette when raised to its highest point and is partially filled with mercury. The volume is obtained by placing the briquette in the reservoir, causing a rise in the level of the mercury in both limbs of the 'U' tube. The burette is then lowered until the mercury has resumed its former level, this movement being the measure of the volume which is read directly from the graduations on the burette."

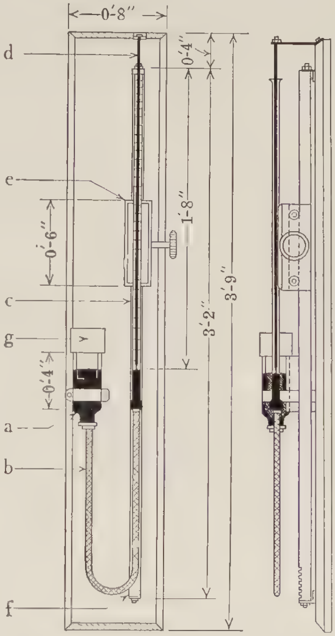

Fig. 70.—Goodner mercury volumeter. (Jour. Amer. Ceram. Soc. IV, 1921.)

The advantages claimed are no soaking of briquette in kerosene necessary, nor draining of briquette or liquid. Directness of reading, speed, and accuracy. The disadvantages are: Initial cost of mercury, tendency of latter to remain in small holes or cracks of test-piece though readily shaken off, and slight difficulty in obtaining readings for the first dozen determinations made with the apparatus.

Volumeter for air determination.—Figure 71 shows a simple type of volumeter designed by H. Spurrier.[3] To operate the apparatus test-pieces are used which can be placed in the bell of the funnel. In a one liter beaker put 800 c.c. of water and boil for some time. The funnel with stopcock open is placed in beaker, and by means of a rubber tube attached to inverted tip of burette cock, water is sucked up until it fills apparatus to bore of cock. Close cock. Raise bell high enough to place test-piece in water. As clay slakes evolution of air goes on and collects in upper part of burette, so that its volume can be measured. The percentage volume of air is calculated on basis of volume of the test-piece used.

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[1] See also Washburn and Bunting, Jour. Amer. Ceram. Soc., V, p. 394, 1922.

[2] Goodner, E. F., Jour. Amer. Ceram. Soc., IV, p. 289, 1921.

[3] Jour. Amer. Ceram. Soc., II, p. 490, 1918.

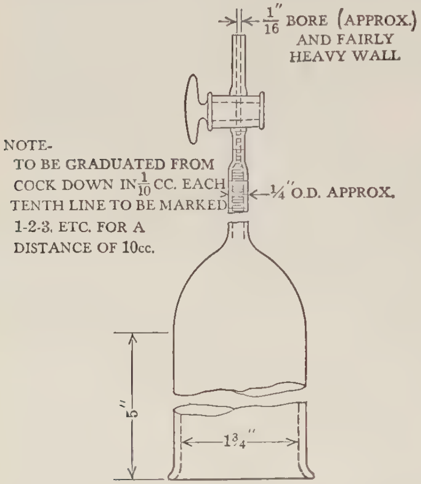
$\frac{1}{16}''$ BORE (APPROX.) AND FAIRLY HEAVY WALL
NOTE- TO BE GRADUATED FROM COCK DOWN IN $\frac{1}{10}$ CC. EACH TENTH LINE TO BE MARKED 1-2-3, ETC. FOR A DISTANCE OF 10cc.
¼" O.D. APPROX.
5"
1¾"

Fig. 71.—Spurrier's apparatus for determination of air in clay. (Jour. Amer. Ceram. Soc., II, 1919.)

Porosity

The porosity of a clay may be defined as the volume of the porespace between the clay particles, expressed in percentages of the total volume of the clay, and depends on the shape and size of the particles making up the mass.

In raw clays the pores are all open although some of them may be exceedingly small.

In fired clays the pores may be of variable size, but are of two types, open and closed. The volume of the latter which form by the expansion of liberated gases during fusion cannot be directly measured. There is no doubt also that pores may vary greatly in their shape.

Effect of porosity.—In the raw clay the possible rate of safe drying depends on the amount of water absorbed and the facility with which it can escape; large pores permitting the water to escape rapidly. Small pores, on the other hand, retard both the absorption and evaporation of the water.

Porosity[1] has an important bearing upon the strength of a fired clay body, its behavior as an absorbent, and its resistance to weathering, shock, abrasion, erosion, slagging, temperature strain, discoloring agents, efflorescence, chemical attack by gases and liquids, and the destructive action of fungus growths,[2] as well as its effect on certain properties such as bulk density, dielectric strength, permeability, and thermal and electrical conductivity.

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[1] Washburn, E. W., Jour. Amer. Ceram. Soc., IV, p. 916, 1921.

[2] Scott, F., Brit. Clayw., XVIII, p. 138, 1920.

While the amount of pressure on a plastic mass does not seem to affect the porosity of the unfired clay, there will of course be a difference in a clay pressed plastic and dry pressed, and this will also show in the fired material, when both are heated to the same temperature. Thus in the case of some briquettes made of Canton, Ohio, shale and fired to 1030° C., the porosity was 22.8 per cent for the dry-pressed, and 16.8 per cent for the plastic-molded. The per cent porosity also decreased very rapidly with an increase in temperature for the plastic-molded ones, becoming practically 0 per cent at 1150° C., while the dry-pressed pieces at this temperature still showed nearly 5 per cent porosity.[1]

Parmelee [2] found little difference, however, in the porosity of a clay fired to cone 6, and molded with pressure ranging from hand to 50,000 lbs. per square inch.

Porosity and vitrification.—Purdy [3] and others have called attention to the fact that the porosity-temperature relation in burning serves as an important criterion for determining the commercial use of the clay. Figures 72 and 73 show a series of curves constructed by Purdy on the basis of his study of Illinois clays. While these curves are very suggestive they must of course be regarded as approximate.

It is evident that decrease in porosity shows the progress of hardening and vitrification in the material during firing. Clays showing a sharp drop in porosity, due to sudden fluxing action vitrify rapidly, and where a rise in the porosity curve quickly succeeds the drop in porosity, it indicates a short firing range. Changes parallel with the porosity, occur in the specific gravity (*q. v.*).

Fluxes, of course, affect the porosity since they tend to promote vitrification.[4]

Types of porosity.—Two types of porosity are recognized, viz.: *true* and *apparent.*

The true porosity would represent the volume of the open plus the closed pores.

The apparent porosity is that expressed by the volume of the open pores.

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[1] Bleininger, A. V., and Montgomery, E. T., U. S. Bur. Stand., Tech. Pap. 22, and Bleininger, Trans. Amer. Ceram. Soc., XV, p. 570, 1913.

[2] Jour. Amer. Ceram. Soc., XVI, p. 195, 1914.

[3] Ill. Geol. Surv., Bull. 9, p. 270, 1908.

[4] See Bleininger and Moore, Trans. Amer. Ceram. Soc., X, p. 313, 1908; Keele, ibid., XIII, p. 731, 1911.

Determination of porosity.—Apparent porosity may be determined by the following formula, when weighing the test-piece in water.

$$A.\ P. = \frac{(W - D)100}{W - S},$$

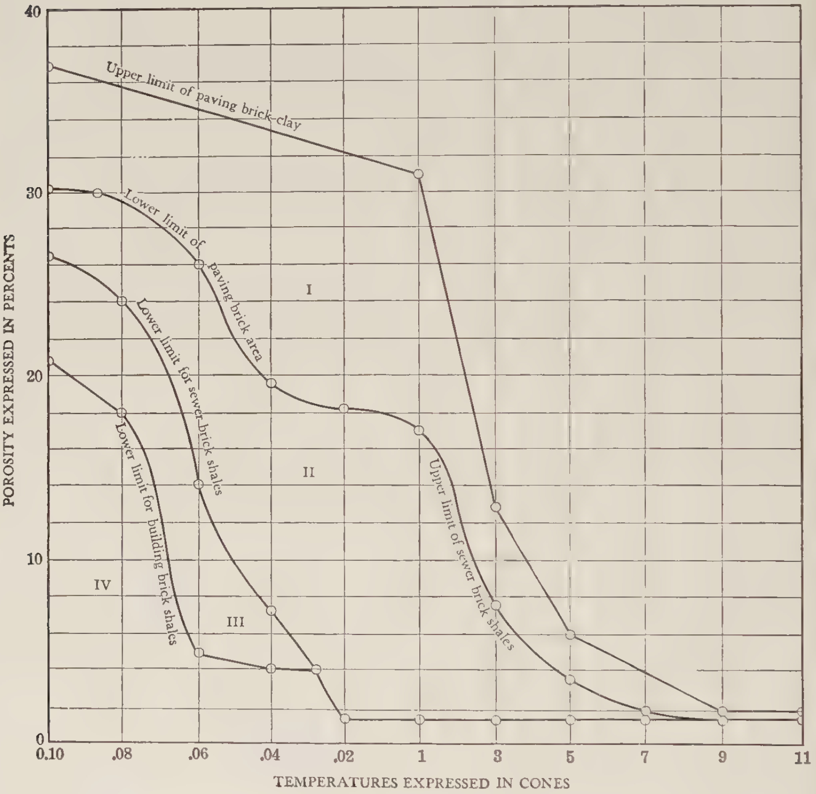

FIG. 72.—Differentiation of fire clays on basis of porosity changes. (Purdy, Ill. Geol. Surv., Bull. 9, 1908.)

I. Area of clays suitable for first-class pavers; II. Area of clays not suitable for first-class pavers, but good for vitrified front brick and hollow block; III. Area of clays with short heat range, and suitable only for porous products, as common brick, and porous hollow ware; IV. Area of clays unsuited for manufacturing purposes.

W = weight of the saturated briquette;
D = weight of dry briquette;
S = weight of saturated briquette suspended in water.

Closed pores should be expressed in terms of true clay volume.

The calculations given in tentative specifications of the American Ceramic Society are as follows:

$$\frac{\text{Dry wt. in grams}}{\text{True sp. gr.}} = \text{True clay volume in c.c.}$$

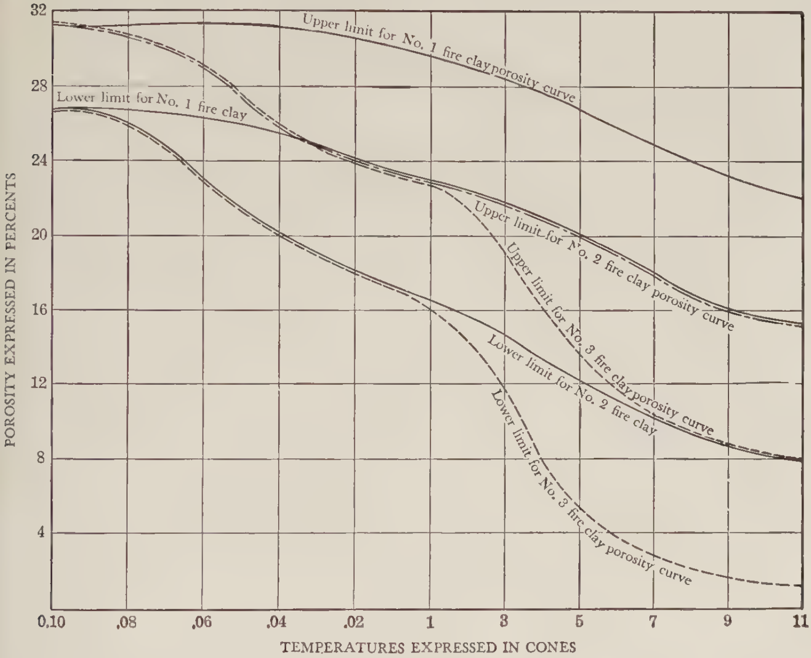

FIG. 73.—Curves showing changes in porosity of paving and building brick clays with progressive intensity of heat treatment. (Purdy, Ill. Geol. Surv., Bull. 9, 1908.)

Saturated weight in grams − dry weight in grams = open pores in c.c.

$$\left.\begin{array}{l}\text{Open pores in per cent}\\ \text{true clay volume}\end{array}\right\} = \frac{\text{Sat. wt. in grams} - \text{dry wt. in grams}}{\text{True clay volume in c.c.}}$$

$$\left.\begin{array}{l}\text{Closed pores in}\\ \text{per cent true}\\ \text{clay volume}\end{array}\right\} = \frac{\text{Dry wt. in grams} - \text{susp. wt. in grams} - \dfrac{\text{Dry wt.}}{\text{True sp. gr.}}}{\text{True clay volume.}}$$

or, per cent closed pores = $$\frac{D - S - \frac{D}{T}}{\frac{D}{T}}$$

D = dry weight;
T = true specific gravity;
S = saturated weight.

In making any tests involving the saturation of the test-piece this may be done by soaking it for twenty-four hours in water, and then in boiling water for one hour.

A formula given by Searle[1] for true porosity is:

$$P = 100\left(1 - \frac{W}{SV}\right)$$

P = true porosity in terms of per cent by volume;
W = weight of dry sample;
V = volume of sample;
S = specific gravity of powder.

Purdy[2] suggests the following formula for determining the volume of sealed pores:

$$\text{Sealed pores} = \left(\frac{T - A}{T}\right) \times 100$$

where T is the true specific gravity and A = apparent specific gravity.

Method of submersion.—Washburn[3] claims that the ordinary immersion method has been shown to be unreliable, and so too is simple immersion in low *vacuo*. Furthermore, depending upon the humidity of the atmosphere, adsorbed water may cause errors up to 2 per cent in the porosity value. He points out that perfectly dry fired clay will remove water from conc. H_2SO_4 and from fused $CaCl_2$.

He also states one hour boiling failed to saturate completely. Continued boiling, he points out, shows that the saturated weight increases linearly with the time, even though appreciable quantities of dissolved matter are removed from the test-piece by hot water. This Washburn claims is due to gradual and continuous rehydration of the clay by the hot water. The error from this factor may amount to as much as 3 per cent, and that from dissolved materials to as much as 2 per cent, during a three hours' boiling.[1]

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[1] Chemistry and Physics of Clays, p. 83.

[2] Jour. Amer. Ceram. Soc., XI, p. 60, 1909.

[3] Jour. Amer. Ceram. Soc., IV, p. 961, 1921.

The following figures are given by Washburn:

INFLUENCE OF ATMOSPHERIC HUMIDITY ON "DRY WEIGHT" OF CLAY BODIES. PERCENTAGE OF GAIN IN WEIGHT ON STANDING

Drawing temperature	PERCENTAGE GAIN IN WEIGHT ON STANDING						
	After 24 hours 0 per cent saturated air	After 24 hours 33 per cent saturated air	After 24 hours 100 per cent saturated air	After 48 hours 100 per cent saturated air	After 72 hours 100 per cent saturated air	After 96 hours 100 per cent saturated air	After 120 hours 100 per cent saturated air
950°C.	80.370	0.071	0.27	0.32	0.42	0.44	0.46
1050°C.	84.061	0.080	0.57	0.87	0.97	1.08	1.12
1150°C.	83.149	0.008	0.02	0.05	0.05	0.06	0.07

COMPARISON OF THE "BOILING-IN-VACUO" AND THE "BOILING-IN-AIR" METHODS FOR DETERMINING THE POROSITY OF BURNED CLAY BODIES

Drawing temperature	Dry weight in grams	Weight after boiling 1 hour at 25 °	Per cent of gain in weight	Weight after boiling an additional hour at 100° C.	Additional per cent of gain	Weight after drying *in vacuo* at 100° followed by 1 hour boiling at 100°	Per cent of gain over original dry weight	Weight after two additional hours boiling at 100° C.	Additional per cent of gain	Total per cent of gain	Dry weight after removal in water *in vacuo* at 110°
950°C.	80.41	101.306	26.0	101.329	0.03	100.695	25.2	101.272	0.7	25.9	81.757
1050°C.	83.914	102.730	22.4	102.763	0.04	102.211	21.8	102.801	0.7	22.5	84.187
1150°C.	84.33	89.876	6.59	89.957	0.69	89.318	5.91	89.849	0.6	6.5	84.443

The rehydration of a briquette fired at 1050° C. is illustrated by the following figures given by Washburn.

Dry weight after heating to 1000° and cooling in high *vacuo* 81.265 grams.

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[1] For data on the amount of saturation obtained by different kinds of immersion see Beecher, C. E., Trans. Amer. Ceram. Soc., XVIII, p. 73, 1916; Walker, F. W., Jr., ibid., XVIII, p. 446, 1916; Ries, H., ibid., IX, p. 699, 1907; Purdy and Moore, ibid., IX, p. 211, 1907.

Increase in weight (expressed in per cent of dry weight) produced by:

Standing 12 hours over calcium chloride	0.04
Standing 72 hours over water	0.47
Standing 92 hours over water	0.53
Boiling 24 hours in water at 100° C.	22.40
Boiling 72 hours in water at 100° C.	22.60
Boiling 456 hours in water at 100° C.	22.90
Loss of dissolved material	0.36
The above treatment followed by drying in *vacuo*, 110° C., 3 hours	0.91
Plus material dissolved	1.27
The above treatment followed by two ignitions at red heat	0.20

Washburn[1] recommends that some petroleum product be used as an immersion liquid instead of water, expressing preference for vaseline, which has a high fluidity when hot. The use of this he claims has the following advantages: 1. Absence of slaking action on raw clay; 2. Little, if any, solvent action on the constituents of the body; 3. No tendency to combine chemically with the constituents of the body; and 4. Much less tendency to be adsorbed on the surface. The following three sets of figures are given by him:

DETERMINATION OF PORE VOLUME IN C.C. WITH WATER AND VASELINE

	With water	With vaseline	Difference, per cent
Briquette 1	8.22	8.40	2.2
Briquette 2	9.22	9.41	2.7
Porous tile	4.48	4.54	1.3

Porosimeters.—The porosity of clay bodies may be determined with an apparatus known as the porosimeter, in which either the liquid absorption or the principle of gas expansion may be used.

Seger volumeter.—The porosity of the clay in either its raw or burned condition may be determined by means of a Seger volumeter described under Shrinkage. The porosity percentage is determined by the formula

$$P = \frac{\frac{g}{s}}{V} \times 100,$$

in which V = volume of wet test-piece;
g = difference in weight between dry and saturated test-piece or the weight in grams of oil absorbed;
s = specific gravity of oil.

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[1] Jour. Amer. Ceram. Soc., IV. p. 983, 1921.

In testing the porosity of burned wares distilled water can be used.

Gas-expansion porosimeter.—In this a gas instead of liquid is used to fill the pores of the test-piece. The amount of gas is determined by measuring the change of pressure which accompanies a definite increase in volume.

It is then possible to calculate either the solid or pore volume of the test-piece.

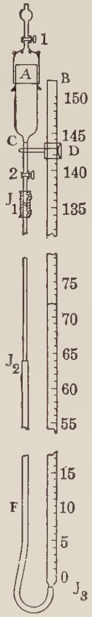

Fig. 74.—Washburn and Bunting porosimeter. (Jour. Amer. Ceram. Soc., V, 1922.)

Bulk volume is determined by direct measurement of liquid displacement.

Washburn and Bunting porosimeter.—The principle of this depends on allowing the gas which fills the pores of a body to expand into a measured volume, and measuring the accompanying fall of pressure.[1]

It is claimed that the results obtained by this method are in all cases higher, and sometimes much higher than those obtained by methods of liquid absorption. "The porosimeter (Figs. 74, 75) consists of a porosity bulb, *A*, connected by an impervious rigid-walled flexible tube, *F*, to the burette, *B*, which is provided with a movable reading arm, *D*. The burette is of uniform bore and is accurately graduated in centimeters and millimeters. Its internal cross section should preferably be chosen so as to be close to one square centimeter or some even multiple or submultiple thereof."

"The porosity bulb shown in detail in Fig. 75 consists of a vessel just large enough to admit an unfired test-piece of standard dimensions. The hooks on the outside allow the cap to be held tightly in place by means of rubber bands or spring clamps. The small projections on the inside of the cap are for the purpose of preventing the closure of the outlet tube by the test-piece as it is lifted by admission of mercury."

"The cap and both stopcocks must be well ground and fitted so that the bulb will hold a vacuum for at least 15 minutes without leakage greater than the equivalent of 0.1 mm. of mercury."

"The piece *R* is a solid glass rod, called the *reference piece*, whose volume *Vr*, is accurately determined by weighing it suspended in a liquid."

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[1] Washburn, E. W., and Bunting, E. N., Jour. Amer. Ceram. Soc., V, p. 113, 1922.

“Clean the porosity bulb and burette. Lubricate all ground joints. Connect the apparatus as shown in Fig. 74, and wire each connection tightly. Place in the porosity bulb the reference piece *R*, whose volume $V_R = (1 - s)V_d$, where V_d is the bulk volume of the test-piece, and *s* is the maximum fractional shrinkage which must be provided for. Place the cap on the porosity bulb and secure it. Then raise the burette until its zero mark is on a level with stopcock 1. Open both stopcocks and pour clean mercury into burette until porosity bulb is full.”

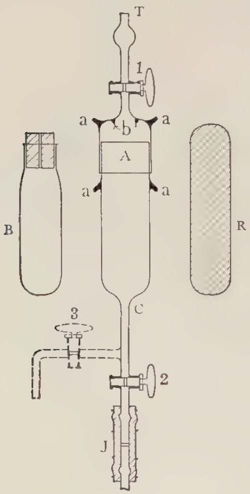

Fig. 75.—Porosity bulb of Washburn and Bunting porosimeter. (Jour. Amer. Ceram. Soc., V, 1922.)

The determination of volume of porosity bulb need be made but once, and as follows: “With reference piece in place and both stopcocks open, raise the burette until mercury just fills porosity bulb up to and into stopcock 1. Close both stopcocks and lower the burette until the mercury surface is approximately level with the mark *C* (Fig. 74). Read the burette R_1. Open stopcock 2, and lower the burette until the mercury level in the porosity bulb coincides with mark *C*. Close stopcock 2 and raise the burette until the mercury surface is again approximately level with the mark *C*. Read the burette R_2.

The difference between the two burette readings, $R_2 - R_1$, is the free volume V_F, of the porosity bulb when it contains the reference piece.”

“Open stopcock 1 and remove the reference piece. Open stopcock 2 and again raise the burette until the mercury level stands approximately at its zero mark. Close stopcock 2, lower the burette until the mercury surface in it is on the level of mark *C* and read again, R_3. Now pour out the mercury in the porosity bulb until the level falls to mark *C*. Collect and weigh this mercury, M_m grams.

“The volume V_1 of the porosity bulb may now be computed, in burette, scale units, from the relation

$$V = V_F + \frac{V_R(R_2 - R_3)D_m}{M_m}$$

where D_m is the density of the mercury at the room temperature prevailing.”

To determine porosity. "With the test-piece in place raise the burette until the mercury fills the porosity bulb up to some point within the bore of stopcock 1. Read the burette R_0. Then close stopcock 1. Lower the burette until the mercury level in the bulb stands at mark C. Clamp the burette, set the reading arm on the level of the mercury surface at C and read its position on the burette R'_c. Then read the position of mercury surface in burette R'_m. Adjust until mercury level at C remains constant.

"When R'_c and R'_m have been determined, close stopcock 2 and raise the burette until the mercury level in it is approximately level with mark C and read the burette R.

"The per cent porosity is computed from the relation

$$\frac{X}{100} = \frac{[B - (R'_c - R'_m)](R - R_0)}{(R'_c - R'_m + \triangle)[V - (R - R_0)]}$$

"The small capillary depression correction $\triangle$, is a constant for a given apparatus and may be determined as follows: With both stopcocks open raise the burette until the mercury stands at mark C. The difference in the two mercury levels is the quantity $\triangle$."

The principle used by Washburn and Bunting[1] has been employed also for making a porosimeter suitable for testing brick.[2]

Navias[3] devised a stronger type, which also involved direct pore volume reading. The bulk volume still has to be determined in a separate apparatus.

MacGee direct-reading gas expansion porosimeter.—The apparatus,[4] Fig. 76, consists of the following parts: B, container for sample, about $4\frac{3}{4}$ inches long and $1\frac{1}{4}$ inches internal diameter, with exactly 100 c.c. volume from A–Z; C, an ordinary 100 c.c. burette, with 100 c.c. mark at Z; D, burette of about 200 c.c. capacity, and lower 100 c.c. calibrated; E, meter stick calibrated in millimeters for measuring pressure differences in C and D; G, flexible metal-covered rubber tube.

Operation.—Put sufficient dry, clean mercury in apparatus to cause levels to stand at Z and F. Place sample in B, and clamp on cover with rubber bands. Open stopcock A. Raise D until mercury level in C is at Z. Close stopcock. Lower D until pressure difference between C and D is one-half of atmospheric as read on E. Read burette C, this being the solid volume S of test-piece. Open stopcock. Raise D, this reading being bulk volume b of test-piece.

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[1] Jour. Amer. Ceram. Soc., V, p. 535, 1922.

[2] Bole and Jackson, Brick and Clay Rec., LXI, p. 314, 1922, and Pressler, E. E., Jour. Amer. Ceram. Soc., VII, p. 154, 1924.

[3] Jour. Amer. Ceram. Soc., VIII, p. 816, 1925.

[4] Jour. Amer. Ceram. Soc., IX, p. 814, 1926.

$$\text{Porosity in per cent} = \frac{b - s}{b} \times 100.$$

$$\text{The apparent specific gravity} = \frac{\text{dry weight of test-piece}}{\text{solid volume}}.$$

Porosimeter for bricks.—Washburn and Bunting first described an apparatus for determining porosity of full-sized brick by the air-expansion method.

Later a more convenient apparatus was developed by Bole and Jackson.[1] Pressler [2] at a still later date designed an all-metal apparatus.

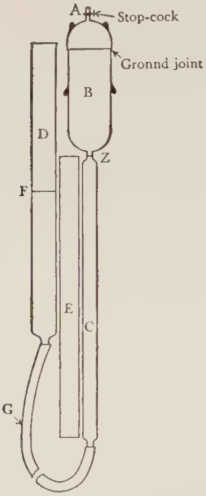

FIG. 76.—MacGee's porosimeter. (Jour. Amer. Ceram. Soc., IX, 1926.)

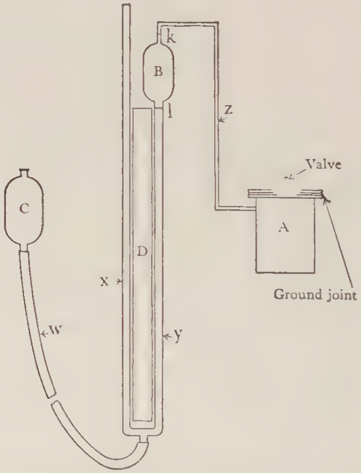

FIG. 77.—MacGee porosimeter for bricks. (Jour. Amer. Ceram. Soc., IX, 1926.)

Still another type has been described by Hartman, Westmont and Morgan,[3] which is said to add considerably to the precision of values obtained on badly distorted brick.

An apparatus described by MacGee [4] is intended to eliminate the use of a vacuum pump required for the others. It is shown in Fig. 77, in which: A, represents a container of rolled steel plate slightly larger than a standard refractory brick. A cover of steel plate is clamped on with wingnut bolts, and made air-tight with a rubber gasket. *B* is an expansion bulb with about 250 c.c. capacity; *C* is a leveling bulb; *D*, a meter stick; *x*; the manometer *y* is of glass tubing of 5 mm. internal diameter; *w* is heavy-walled rubber tubing; *z* is capillary glass tube.

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[1] Brick and Clay Rec., LXI, p. 314, 1922.

[2] Jour. Amer. Ceram. Soc., V, p. 154, 1924.

[3] Jour. Amer. Ceram. Soc., IX, p. 298, 1926.

[4] Jour. Amer. Ceram. Soc., IX, p. 819, 1926.

Place sufficient mercury in leveling bulb *C* to fill *B* to the mark *K*. Put brick in *A* and clamp on cover.

To operate: 1. Raise *C* until mercury in *B* is at level *K*. Close valve. 2. Lower *C* until mercury stands at level *L*. 3. Read pressure difference between *x* and *y* on *D*. The reading, *R*, of *D* (as determined under 3 above) is subtracted from the barometric pressure in order to obtain the pressure *P* after the expansion process described under 1 and 2 above.

Air space a, in $A = \dfrac{p \times B}{R}$.

B is volume from K to L.

Solid volume, s, of test-piece $= A - a$.

A is volume of the sample container.

Porosity in per cent $= \dfrac{v - s}{v} \times 100$.

The bulk volume, *v*, of brick is determined by direct measurement with a meter stick, the average of several readings in each dimension being taken.

For apparent specific gravity divide *w* (dry weight of brick) by solid volume.

SPECIFIC GRAVITY

The specific gravity of a clay may be expressed in three different ways, as follows:

1. Apparent specific gravity, which represents the ratio of the volume of the solids plus the volume of the closed pores to an equal volume of water.

2. Bulk specific gravity, representing the ratio of the entire volume of the material, including solids, closed, and open pores, to an equal volume of water. Searle [1] suggests calling this the apparent density.

3. True specific gravity, or the ratio of the solid material, exclusive of closed or open pores, to an equal volume of water. In order to eliminate any closed pores, the true specific gravity should be determined on a powdered sample.

Factors influencing specific gravity.—The true specific gravity of a raw clay will be influenced by the minerals which it contains in abundance, and yet the specific gravity of these varies but little as can be seen from the following figures: Kaolinite, 2.6; quartz, 2.65; feldspar, 2.55-2.75; muscovite, 2.76–3.0; biotite, 2.7–3.1; calcite, 2.71.

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[1] Chemistry and Physics of clays.

The apparent and bulk specific gravity of dry unfired clay will be affected both by its porosity and the true specific gravity of the minerals composing it.

In fired clays the true specific gravity is affected by at least four factors, viz.: 1. Inversion of silica; 2. Fusion; 3. Chemical reactions; and 4. Crystallization.

The apparent and bulk specific gravity are affected by all four of these, and in addition by porosity and the formation of "blebs."

Use of specific gravity.—Specific gravity is of value for determining the weight of a raw clay per unit volume.

It also serves as an index of the process of vitrification taking place during firing.[1]

The specific gravity may furthermore be of service in determining the correct consistency of a slip, indicating whether it is too thick or too thin.

Specific gravity of clay.—A number of true and apparent specific gravity determinations by different writers are given below:

SPECIFIC GRAVITY OF RAW CLAY

New Jersey *	2.34–2.84
Iowa †	2.32–2.64
Missouri ‡	1.66–2.60
New Jersey §	1.80–2.60

* Ries, H., N. J. Geol. Surv., Fin. Rept., VI, p. 114, 1904.
† Beyer, S. W., and Williams, I. A., Iowa Geol. Surv., XIV, p. 116, 1904.
‡ Wheeler, H. A., Mo. Geol. Surv., XI, p. 562, 1896.
§ Smock, J. C., N. J. Geol. Surv., Rept. on Clays, 1878.

Some of the recorded specific gravities noted above fall considerably below the average of the common minerals found in clay, which may be due to the method of determination used.

This no doubt explains the lower values obtained by Wheeler and Smock, as the method used by them consisted in coating a lump of clay with paraffin so that it could not slack in water, and then determining the suspended weight of this lump in the liquid. This is really the bulk specific gravity.

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[1] Purdy, R. C., Ill. Geol. Surv., Bull. IX, p. 133, 1908; Bleininger and Moore, Trans. Amer. Ceram. Soc., X, p. 293, 1908.

The differences obtained by the two methods have been well brought out by a series of tests on West Virginia clays given below:[1]

APPARENT AND TRUE SPECIFIC GRAVITY OF CLAYS

Clay	Apparent specific gravity	Porosity	Real specific gravity	
			Calculated	Pycnometer
Point Pleasant River clay	1.75	30.2	2.51	
Barboursville clay	1.68	29.1	2.37	
Clarksburg clay	1.92	23.8	2.52	
Morgantown shale	1.86	25.5	2.49	
Morgantown shale	1.88	26.1	2.53	
Bridgeport pottery clay	1.76	25.1	2.35	
Thornton plastic clay	1.84	23.6	2.41	
Thornton flint clay	1.94	25.8	2.61	
Hammond flint clay	1.71	26.5	2.34	2.57
Charlestown River clay	1.88	29.4	2.66	2.61

Apparent specific gravity of powdered clay.—Weigel[2] in referring to the use of clay as a filler, says:

"The apparent specific gravity or weight per unit volume of the dry pulverized clay is a property whose value, as determining the best use of the clay, is doubtful. It is a measure of the fluffiness or packing qualities of the powdered clay under its own weight. It apparently has no relation to the other physical properties, with the exception of oil absorption." The figures obtained show that to some extent the oil absorption varies inversely as the weight per unit volume.

"The apparent specific gravity of the powdered clay "was determined by a Scott volumeter, which consists of a series of small glass baffles, one above the other, set at such an angle that the powdered clay will slide freely from the lower edge of one to the top of the other. The clay, dried at 105° C., and then cooled under atmospheric conditions, is fed into the top baffle through a 20-mesh screen to break up any lumps. The bottom baffle discharges into a short funnel, under which is a cubical measure holding exactly 1 cubic inch. The measure is allowed to fill completely and run over. It is then struck off with the edge of a stiff spatula and weighed." .

Specific gravity changes on firing.—It has already been pointed out that the specific gravity of a clay may change on firing.[3]

[1] W. Va. Geol. Surv., p. 65, 1906.

[2] U. S. Bur. Mines, Tech. Pap. 243, 1925.

[3] For information on the specific gravity of fired clays see: Md. Geol. Surv., XI, Pt. II, 1922; Ill. Geol Surv., Bull. 9; Jour. Soc. Glass Technol., IV, p. 162, 201, 265 and 397, 1920; Trans. Amer. Ceram. Soc., X, p. 273, 313 and 360, 1908; XV, p. 71, 1913; U. S. Bur. Mines, Tech. Pap. 233, 1920; U. S. Bur. Stand., Tech. Pap. 22; Jour. Amer. Ceram. Soc., V, p. 278, 1922; Jour. Frank, Inst., CLXXXIII p. 127, 1917; U. S. Bur. Stand., Tech. Pap. 227.

Clays may show a slight increase in true specific gravity af
dration, but above that both the true and apparent specific g
general decrease.

Bulk specific gravity in fired clay is less than apparent, and i
increases up to vitrification, but decreases beyond this point.

The slight increase that has been noticed around the deh

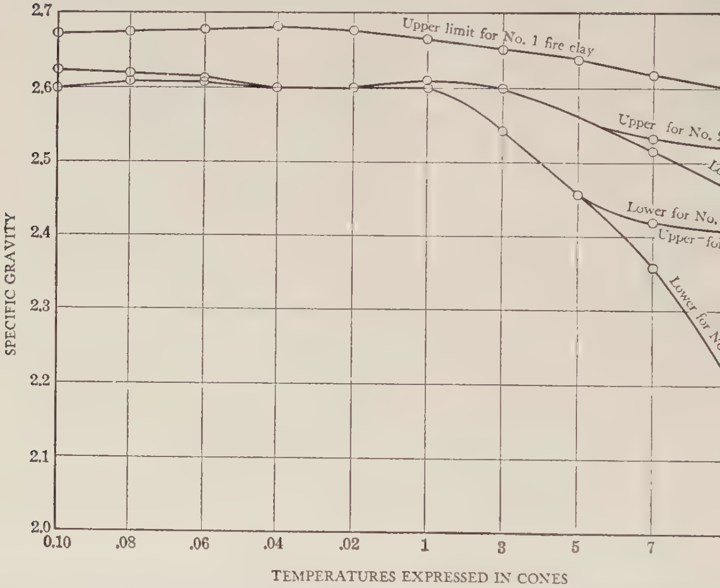

FIG. 78.—Curve showing changes in specific gravity (apparent), of paving
ing brick clays with progressive intensity of heat treatment. (Purdy,
Surv., Bull. 9, 1908.)

temperature has been thought by some to be due to a chang
constitution of the kaolinite molecule.[1]

Most silicates increase in volume on fusing, and this would
decrease the density on firing.[2] Thus feldspar in its crystalli
gave 2.611, and fused 2.467.

Changes in volume may also be brought about by invers
from quartz to tridymite (2.654 to 2.326), and by changes in pore
Crystallization, as the formation of mullite, has been advanced as
reason. The presence of fluxes, since they promote fusion, wo
tend to reduce true and apparent specific gravity.

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[1] Green and Theobald, Trans. Ceram. Soc. (Eng.), XXIV, p. 129,
Knote, Trans. Amer. Ceram. Soc., XII, p. 226, 1910.

[2] Green and Theobald, Trans. Ceram. Soc. (Eng.), XXIV, p. 129,
Laurent, Ann. Chim. Phys., II, p. 66 and 96, 1837; Rose, Pogg. Ann
p. 97, 1845; Brogniart, Traité des arts céramique, I, p. 283 and 720, 1877.

It is also asserted [1] that the more rapid the fall in specific gravity during firing, the more rapid will be vitrification, and the shorter the vitrification range. Purdy suggests the use of apparent specific gravity curves to indicate the behavior of a clay during firing (Fig. 78).

Specific gravity determinations of fired clays.—A number of specific gravity determinations of fired clays have been published, but the series is usually incomplete so far as temperature range, and the determination of all three types of gravity are concerned.

The following table gives the true specific gravity of ten clays heated from 200° C. to 700° C.[2]

TRUE SPECIFIC GRAVITY OF SEVERAL CLAYS AFTER HEATING 4 TO 6 HOURS AT INDICATED TEMPERATURES

Clay	200°	400°	450°	500°	550°	600°	650°	700°
North Carolina kaolin...	2.60	2.570	2.480	2.440	2.480	2.485	2.490	2.490
Georgia kaolin.........	2.60	2.580	2.520	2.460	2.485	2.490	2.500	2.490
Tennessee ball clay.....	2.65	2.640	2.630	2.530	2.590	2.600	2.590	2.600
Ohio fire clay..........	2.72	2.720	2.710	2.570	2.580	2.580	2.580	2.580
Maryland fire clay......	2.69	2.685	2.650	2.570	2.610	2.605	2.615	2.615
Maryland flint clay.....	2.62	2.600	2.550	2.475	2.500	2.530	2.560	2.580
Ohio shale.............	2.79	2.750	2.730	2.720	2.710	2.700	2.710	2.710
Illinois shale..........	2.74	2.750	2.750	2.730	2.715	2.715	2.700	2.705
Ohio surface clay.......	2.755	2.765	2.730	2.700	2.690	2.690	2.670	2.675
Georgia surface clay....	2.625	2.650	2.565	2.555	2.595	2.610	2.615	2.625

Worcester gives the apparent specific gravity [3] of a series of roofing-tile clays heated from cone 010 to cone 5. In all of these the apparent specific gravity in general decreases. In those showing a reduction which is moderate in amount, and occurring sufficiently late in the firing, the vitrification range is regarded as wide and safe. In those of unsafe vitrification habit, the reduction is large and rapid. Two examples of each group are given below:

APPARENT SPECIFIC GRAVITY CHANGES IN ROOFING TILE CLAYS

Cone	010	08	06	04	02	1	2	3	4	5
Good vitrification...	2.68	2.69	2.68	2.67	2.57	2.62	2.53	2.54	2.51	2.35
	2.50	2.53	2.52	2.50	2.48	2.45	2.45	2.44	2.42	2.13
Unsafe vitrification.	2.60	2.58	2.55	2.58	2.52	2.42	2.50	2.32	1.93	1.73
	2.61	2.54	2.62	2.59	2.63	2.51	2.35	2.27	1.15	1.20

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[1] Bleininger and Moore, Trans. Amer. Ceram. Soc., X, p. 313, 1918.

[2] Brown, G. H., and Montgomery, E. T., U. S. Bur. Stand., Tech. Pap. 21, p. 14, 1913.

[3] Ohio Geol. Surv., 4th Ser., Bull. 11, p. 122, 1910.

The table below gives a comparison of changes in porosity, volume, apparent and bulk specific gravity of two Maryland plastic fire-clays.[1]

CHANGES IN BULK SPECIFIC, ETC., ON HEATING, OF SOME MARYLAND CLAYS

Temperature	1150° C.	1200° C.	1250° C.	1275° C.	1300° C.	1325° C.	1350° C.	1375° C.	1400° C.
Porosity	22.8	22.0	10.1	9.6	6.6	6.3	1.4	0.7	0.4
Volume of shrinkage	8.0	8.9	19.1	20.8	17.6	16.1	19.3	19.5	19.5
Apparent specific gravity	2.52	2.51	2.42	2.44	2.32	2.29	2.24	2.25	2.25
Bulk specific gravity	1.94	1.96	2.18	2.21	2.17	2.14	2.22	2.23	2.24
Porosity	12.1	2.8	2.2	1.4	0.8	2.1	6.0	10.1	11.1
Volume of shrinkage	22.8	28.0	26.9	25.9	27.6	24.3	19.2	14.8	12.6
Apparent specific gravity	2.44	2.36	2.34	2.30	2.29	2.25	2.18	2.17	2.13
Bulk specific gravity	2.15	2.29	2.29	2.27	2.28	2.18	2.05	1.98	1.89

In the following table giving specific gravity determinations of several Illinois clays, No. I is a paving-brick clay from Alton; No. II, a fire-clay; No. III, a fire-clay.

TRUE SPECIFIC GRAVITY AND POROSITY OF FIRED CLAYS *

Cone	I		II		III	
	Porosity	True specific gravity	Porosity	True specific gravity	Porosity	True specific gravity
010	36.9	2.69	30.8	2.64	27.0	2.62
08	36.1	2.67	31.3	2.68	27.3	2.63
06	33.1	2.68	28.5	2.76	27.0	2.64
04	29.5	2.65	24.6	2.63	25.3	2.63
02	24.7	2.635	22.9	2.63	22.8	2.64
1	28.0	2.53	21.9	2.63	24.9	2.64
3	20.0	2.60	14.35	2.53	24.1	2.62
5	7.4	2.29	9.5	....	24.3	2.59
7	5.6	2.15	4.47	2.35	20.4	2.39
9	2.2	1.72	3.97	2.21	18.4	2.46
11	....	....	....	....	16.5	2.46

* Rolfe, Purdy, Talbot and Baker, Ill. Geol. Surv., Bull. 9, p. 268, 1908.

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[1] Md. Geol. Surv., XI, Pt. II, pp. 17 and 22, 1922.

Bulk and True Specific Gravity of Some English Fire Clays *

Temperature, ° C.	I			II		
	Bulk specific gravity	True specific gravity	Porosity, per cent	Bulk specific gravity	True specific gravity	Porosity, per cent
800	1.72	2.60	33.7	1.68	2.40	30.0
900	1.74	2.60	32.7	1.66	2.50	32.4
1000	1.76	2.59	31.9	1.77	2.50	29.2
1100	1.87	2.60	28.1	1.85	2.53	26.5
1200	2.07	2.56	19.1	1.96	2.55	23.2
1300	2.07	2.53	18.9	1.77	2.38	25.6
1400	2.40	2.53	5.1	1.58	2.37	33.4
1500	2.16	2.46	12.2	1.66	2.53	34.3
1600	1.88	2.41	22.2	1.80	2.58	30.5

I. Lower Busty Seam, Durham, Eng.

II. Pot clay bed, Sheffield district, Eng. Hugill and Rees, Trans. Ceram. Soc. (Eng.), XXIV, p. 42, 1924–25.

The following figures given by Houldsworth and Cobb[1] show the changes in specific gravity, etc., taking place in a kaolin when heated from 110° to 1000°:

Specific Gravity and Other Changes on Heating Kaolin

Temperature °C	True specific gravity	Bulk specific gravity	Porosity, per cent	Refractive index
110°	2.642	1.403	46.9	1.564
400°	2.642	1.403	46.9	1.564
450°	2.521	1.298	48.5	1.543
500°	2.510	1.270	49.4	1.518
550°	2.511	1.258	49.9	1.516
600°	2.514	1.257	50.0	1.522
650°	2.529	1.252	50.5	1.518
700°	2.542	1.253	50.7	1.522
750°	2.553	1.256	50.8	
800°	2.565	1.259	50.9	1.527
850°	2.568	1.258	51.0	1.532
900°	2.608	1.267	51.4	1.541
950°	2.684	1.299	51.6	1.542
1000°	2.688	1.309	51.3	1.549

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[1] Trans. Ceram. Soc. (Eng.), XXII, p. 344.

Apparent Specific Gravity and Porosity Changes of Portsmouth, O., Flint Fire Clay *

Temperature, ° C.	Apparent specific gravity	Per cent of porosity
760	2.42	26.99
830	2.40	23.91
840	2.46	26.88
912	2.48	26.87
Cone		
010	2.63	29.07
06	2.67	28.61
04	2.68	27.98
02	2.68	28.10
1	2.71	27.90
3	2.65	25.22
5	2.61	21.32
7	2.66	20.10
9	2.69	19.57
11	2.70	18.47
14	2.69	19.04

* Purdy, Trans. Amer. Ceram. Soc., X, p. 369, 1908.

The curious feature of the above figures is that the flint fire-clay increases instead of decreases in its apparent specific gravity as the temperature is raised, and this is accompanied by an actual swelling of the impermeable solid portion. No true specific gravity determinations were made in connection with the above.

Determination of specific gravity.—The apparent specific gravity is determined as follows:

$$\text{A. Sp. gr.} = \frac{D}{D - S}$$

and bulk specific gravity:

$$\text{B. Sp. gr.} = \frac{D}{W - S}$$

D = weight of dry briquette;
W = weight of saturated briquette;
S = weight of suspended saturated briquette.

Other formulae are:

$$\text{Ap. Sp. gr.} = \frac{\text{Dry weight}}{\text{Volume of mass} - (\text{saturated weight} - \text{dry weight})}.$$

Ap. Sp gr. $= \dfrac{Da}{W - S}$ for use with saturating liquid other than water, so "*a*" is specific gravity of saturating liquid.

The true specific gravity may be determined in several different ways:

1. A non-porous solid may be weighed in air, and then weighed suspended in water. Divide the weight in air by the loss when weighed in water.

2. Weigh the test-piece in grams, determine its volume in cubic centimeter. Divide the weight in grams by the volume in cubic centimeter.

3. Grind the sample to a fine powder and determine the true specific gravity with pycnometer bottle. The formula is:

$$\text{True specific gravity} = \frac{W - P}{(W_1 - P) - (W_2 - W)}$$

P = dry weight of the bottle (including stopper);
W = weight of powder and bottle;
W_2 = weight of powder, bottle, and water;
W_1 = weight of bottle, and water.

In using, the powder is introduced dry into the bottle. After weighing, water is introduced to completely fill the bottle, the stopper inserted and the surplus water removed. If the powder contains air, the bottle should be put under an air pump.[1]

To determine the specific gravity of a slip, this can be done by means of a hydrometer, or by the following formula:[2]

$$\text{Sp. gr.} = \frac{\text{Weight of a volume of the slip}}{\text{Weight of an equal of water}}.$$

Color of Clay

Color of unburned clay.—An unburned clay owes its color commonly to some iron compound or carbonaceous matter, more rarely manganese. A clay free from any of these is white.

Carbonaceous matter will color a clay blue, gray, black, or even purplish, depending on the quantity present, 3 per cent being probably sufficient to produce a deep black.

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[1] See also W. Hugill and W. J. Reese, Trans. Eng. Ceram. Soc., XXIV, p. 70, 1925; Schurecht, U. S. Bur. Mines, Tech. Pap. 233, 1920.

[2] Heath and Green, Handbook of Ceramic Calculations, p. 18, 1922.

Iron oxide colors a clay yellow, brown, or red, depending on the form of oxide present. According to some it may also color a clay blue. See under iron oxide. The greenish color may be due to the silicate of iron, and in some clay marls of the Cretaceous it its caused by the mineral glauconite. The iron coloration is, however, often concealed by the black coloration due to carbonaceous matter, and it is sometimes more or less difficult to make even an approximate estimate of the iron content in a clay from its color. Thus, for example, two clays have been noted by the writer [1] which were nearly of the same color and had respectively 3.12 and 12.40 per cent of ferric oxide.

There is often a marked difference in color between the wet and the dry clay, in fact such a difference at times as to make one doubt that they are the same material. The dry clay is usually of a lighter tint.

Color of burned clay.—The color of a raw or unburned clay is not always an indication of the color it will be when burned. Red clays usually burn red; deep-yellow clays may burn buff or red; chocolate ones commonly burn red or reddish brown; white clays burn white or yellowish white; and gray or black ones may burn red, buff, or white. Green ones usually change to red on firing. Calcareous clays are often either red, yellow, or gray, and may burn red at first, but turn cream, yellow, or buff and, as vitrification is approached show a greenish yellow color.

An excess of alumina seems to exert a bleaching effect similar to that of lime.

The vitrification of ferruginous clays yields browns, greens, and blacks, due to the formation of ferrous silicates.[2]

Seger states that the colors which a burned clay may show depend on:

1. The quantity of iron oxide contained in the clay.
2. The other constituents of the clay accompanying the iron (see Alumina and Lime).
3. The composition of the fire-gases during the burning.
4. The degree of vitrification.
5. The temperature at which the clay is burned.

The same author has attempted to classify clays according to their color-burning qualities as follows:[3]

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[1] N. J. Geol. Surv., Final Report, Vol. VI, p. 112, 1904.

[2] Ia. Geol. Surv., Vol. XIV, p. 59, 1904.

[3] Seger's Collected Writings, Vol. I, p. 109.

Group	Character of clay	Color after burning
1	High in alumina and low in iron	White, or nearly so
2	High in alumina and moderate iron contents	Pale yellow to pale buff
3	Low in alumina and high in iron	Red
4	Low in alumina and high in iron and lime	Cream or yellow

The following table of the color of clays is given by Wilson:[1]

COLOR OF CLAYS

Color	Unweathered	Weathered	Fired color
1. White	White kaolins	White	(Numerous exceptions) white
	White diatomaceous earth	White	Usually pink or red
2. Cream	Cream	Cream	Rarely white Usually buff Sometimes red or brown
3. Gray	Neutral gray	Neutral gray	Occasionally white (ball clays) Usually buff Often red and brown
	Blue gray	Blue gray	Usually red Often red and brown
	Blue gray	Brown gray or brown	Usually red or brown
	Brown gray	Gray brown	Usually red or brown
	Green gray	Gray brown	Red and brown
4. Brown	Gray brown	Gray brown	Rarely buff Red and brown
	Red brown	Red brown	Red and brown
	Yellow brown	Yellow brown	Rarely buff Red and brown
5. Red	Red	Red	Red and brown
6. Yellow	Yellow	Yellow	Often buff Usually red and brown
7. Black	Black	Black	Occasionally white Often buff Usually red or brown

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[1] Univ. Wash. Eng. Exper. Sta., Bull. 18, p. 33, 1923.

SLAKING

When a lump of raw clay or shale is immersed under water it falls to pieces or slakes, the process ceasing only when the clay has broken down to a fine powdery mass. The time required for this varies from a few minutes in the case of soft porous clays to several weeks for tough shales, and some may be incompletely disintegrated even after that.

The slaking property is one of some practical importance, as easily slaking clays temper more readily, or if the material is to be washed, it disintegrates more rapidly in the log-washer.

It is also a rough test for distinguishing between clays of high and low strength.

The tentative method recommended by the American Ceramic Society, Committee on Standards,[1] is as follows: "The test-pieces are cubes made of a mixture of 50 per cent by weight, of ground flint, and 50 per cent of the clay to be tested, ground to pass a standard 28-mesh sieve (0.0232 inch hole, 0.0125 inch wire). The flint used is 'potter's flint' and shall all pass a standard 100-mesh sieve (0.0058 inch hole, 0.0042 inch wire). Cubes of 1-inch size are to be cut from this mixture after it is worked to its best plastic consistency.

"These cubes are to be dried at room temperature until air dry, then at a temperature between 65° C. and 75° C. for at least five hours, and finally without cooling, at 110° C. until approximately constant in weight.

"These cubes are placed on a screen having meshes of not less than two per inch, the wire to be not more than $\frac{1}{16}$ inch diameter. The samples on screen should be carefully immersed in water, at 25° C. (±1° C.), (77° F. ± 2° F.), with at least 1 inch water under the test-piece, and not less than $\frac{1}{2}$ inch nor more than 1 inch above it.

"The time required in minutes, for the whole test-piece to slake and to settle through the screen, is to be reported. The average of two determinations should be taken."

CAPILLARITY

For testing the capillary movement of water through clays,[2] Schurecht used an apparatus like that shown in Fig. 79.

The unburned clay test-piece placed in a glass container rests on a filter paper over a copper screen fastened across the bottom of cylinder. The bottom of glass container just touches the water level. The cylinder with the clay is weighed before the test and at frequent intervals to determine the rate of capillary absorption. Aniline dye added to the water more clearly indicates its rise through the clay.

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[1] Issued Jan., 1918.

[2] Jour. Amer. Ceram. Soc., V, p. 930, 1922.

Figure 80 shows the results on a series of clays.[1]

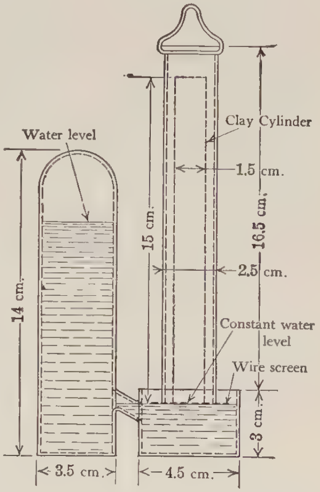

FIG. 79.—Apparatus for measuring the capillary rise of water through clays. (Schurecht, Jour. Amer. Ceram. Soc., V, 1922.)

PERMEABILITY

This term refers to the readiness with which a body will permit liquids or gases to pass through it.

The permeability may be measured by the rate at which some liquid or gas flows through a unit area and unit thickness of body under a unit pressure.[2]

The term permeability should not be confused with porosity, which refers to the volume of pore space.

Two bodies might have the same porosity, but if the pores of one were much smaller its permeability would be lower.

Several different types of apparatus have been devised for determining the permeability of different materials, but there may be some doubt as to whether the results obtained by different methods are in all cases comparable, unless the property is tested under uniform conditions of thickness and area of the test-piece, and uniform pressure. Uniformity of structure throughout the thickness of

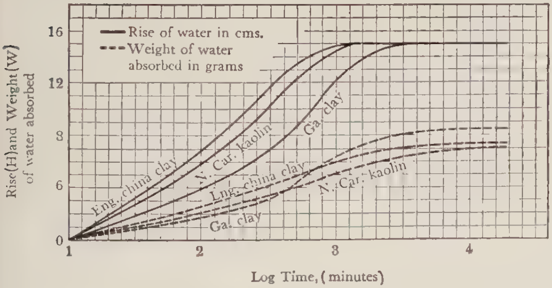

FIG. 80.—Capillary rise and weight of water absorbed by different clays. (Schurecht, Jour. Amer. Ceram. Soc., V, 1922.)

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[1] See also Liesegang and Watanabe, Sprechsaal, LVI, p. 56, 1923, for capillary tests with kaolin.

[2] In this connection see Trans. Amer. Found. Assoc., XXXI, p. 708, 1924; Adams, T. C. Testing Molding Sands to Determine their Permeability, ibid., XXXII, Pt. II, 1925; also Wologdine, Electrochem. Met. Ind., VII, p. 1433, 1909.

the section is also an influencing factor. The last-named factor may be particularly important in unconsolidated materials.

As pointed out by King and Slichter, the permeability of a body is not necessarily a constant, and the permeability may vary with the amount of pressure, and moreover permeability is not a simple function of the dimensions of the specimens.

For unburned ceramic bodies, and even some burned ones, it is better to use air than water, as contact with the latter may change their physical properties.

Among the methods described have been those of King and Slichter,[1] who measured the flow of water and air through sands, and Wologdine,[2] who measured the flow of water through ceramic materials.

Searle [3] has also described two simple types of permeability apparatus, both of which are not altogether satisfactory because the area of the test-piece is larger than section of the water-holding cylinder which is fastened to its top. The liquid therefore in filtering into the brick may spread out laterally.

Another type of permeability apparatus is that recommended by the American Foundrymen's Association.[4] In this, apparatus which is used particularly for sands, a standard test-piece 2 inches in diameter and 2 inches high is used. The air is forced through the specimen by the fall of the bell of a gasometer, and the pressure read on a manometer. The permeability represents the volume of air per minute passing through the specimen, per gram per square centimeter pressure, per unit volume in specimen.

Another type of apparatus has been described by Kessler.[5]

Suction permeameter.—A convenient form of suction type of permeameter is that shown in Fig. 81, and intended especially for determining the permeability of dense bodies.[6]

The pressure used corresponds to 20 cm. of mercury and the specimens used were about 5 mm. thick. The results are expressed in cubic centimeter per minute, measured at pressure corresponding to 560 mm. of mercury, flowing through 1 sq. cm. of a specimen 5 mm. thick under a pressure difference of 20 cm. mercury.

Part *B* has a shallow flare, expanding to about 2.5 cm. in diameter at the bottom, and is ground on the bottom edge so as to fit closely to the specimen E. The specimen is held in place by a short-necked funnel, which is in turn supported on a ring stand I.

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[1] U. S. Geol. Surv., 19th Ann. Rept., Pt. II, p. 899.

[2] Electrochem. and Metallurg. Ind., VII, p. 383 and 433, 1909.

[3] The Chemistry and Physics of Clays and other Ceramic Materials, p. 91, 1924.

[4] Trans. Amer. Found. Assoc., XXXI, p. 708, 1924.

[5] U. S. Bur. Stand., Tech. Pap. 305, 1926.

[6] Ketchum, P. W., Westman, A. E. R., Hursh, R. K., Univ. Ill. Eng. Exper. Sta., Circ. 11, 1926.

The tube C is connected to B and K by ground joints which are provided with mercury cup seals.

Calibration.—The pressure across the specimen is determined by the difference in height of the mercury levels in T and in R. In order to obtain a zero point of pressure on the scale, a fixed point, such as P_1, is chosen on the tube. The reservoir is then adjusted to such a height that when the mercury column is drawn up to P_1, and allowed to run back freely, it will come to rest about half way between P_2 and P_3. With the reservoir adjusted in this way, the reading for zero pressure is taken as the height of the mercury in the reservoir when the mercury column stands at P_1.

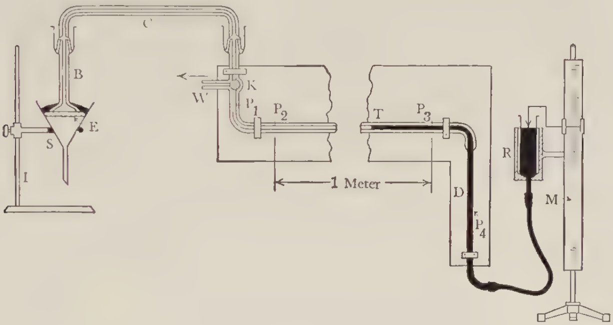

FIG. 81.—Suction permeameter.

C = Capillary tube, 2 mm. bore; K = Three-way stopcock; T = Horizontal capillary measuring tube, 1 m. long; D = Tube of larger bore; R = Mercury reservoir, at least 3 cm. diameter; M = Stand with scale with pointer for measuring height of mercury; W = Connection with water aspirator pump; B = Tube with shallow flare at bottom, and ground-edge to fit specimen E; s = Short necked funnel; I = Ring stand; parts B, C and K connected by ground-glass joints, provided with mercury cup seals.

To obtain the standard pressure difference of 20 cm., the mercury column is maintained at P_1, while the reservoir is lowered until the mercury in it is 20 cm. below the level for zero pressure. Volume v of tube T between P_2 and P_3 is measured by weighing the amount of mercury required to fill this portion of the tube.

Operation.—Part B is removed from the rest of the apparatus by lowering the ring of the support stand, and sealed to specimen E by means of hot beeswax or other suitable material. This combination is then sealed into place in the funnel which, after being cooled to room temperature, is placed in the ring S and raised so as to connect B and C.

A rubber band over S and C prevents the parts from becoming displaced before the vacuum is established. Stopcock K is then turned so as to connect the vacuum pump with both C and T. The pump reduces the pressure in these tubes, thereby causing the mercury column to travel along T from P_2 to P_1. When the column is somewhere near P_1 stopcock K is turned so as to connect only C and T. Due to the passage of air through the specimen, the mercury column will now run back and the time t required for it to go from P_2 to P_1 is measured with a stop-watch.

Calculation of Results.—Area A of the bottom opening of part B may be taken as the effective area of the piece because measurements have shown that the air-flow through the specimen occurs almost entirely along straight lines perpendicular to the surfaces of the piece, as long as the ratio of A to the thickness of the specimen is sufficiently large. For instance, in the present measurements, the diameter of the bottom opening of part B was about five times the thickness of the piece, and the error due to non-linear flow was practically negligible. For higher accuracy, the bottom of the specimen can be waxed so as to expose an area equal and opposite to that exposed above.

It was found by experiment that the time t is directly proportional to the thickness d of the specimen. This relation can also be predicted from theoretical considerations on the assumption that for an infinitesimal element of a capillary tube the velocity of flow is inversely proportional to the length of the element.

The permeability P is therefore given by the expression

$$P = \frac{2vd}{tA}$$

where v is the volume in cubic centimeter of the tube T between P_1 and P_2, d is the thickness of the specimen in centimeter, t is the time in minutes required for the mercury column to go from P_2 to P_1, and A is the area in square centimeter of the bottom opening of the part B. The factor 2 is required because we have chosen 0.5 cm. as the standard thickness (see Section 9). When the same apparatus is used to measure specimens of equal thickness, time t can be taken as a measure of their relative permeability, v, d, and A being constant. To compare permeabilities measured by different type A instruments all operated at nearly 760 mm. barometric pressure, the values of v, d, and A for the different instruments must be taken into account.

Schurecht permeameter.—The permeability of clays to water has been tested by Schurecht in a specially designed apparatus. (Fig. 82.)

The clay to be tested in its plastic condition is mixed with water to normal consistency and then pressed into a cylindrical hole of 1 cm. diameter in the lower rubber stopper. Filter paper is sealed to the paper above and below the clay by means of paraffin,[1] to prevent the clay mixing with water.

The cylinder is filled with distilled water to point indicated, the stopper inserted and the whole weighed. Weights are taken at intervals up to thirty days. The loss in water permits calculation of water passing through clay. The cylinder is refilled to 12.75 cm. level after each weighing.

The chart shows the total grams of water passing through certain clays in a given time (Fig. 83).

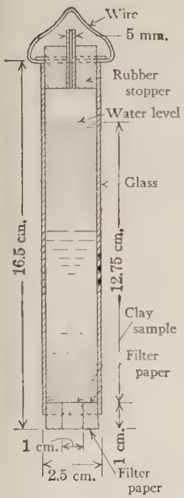

FIG. 82.

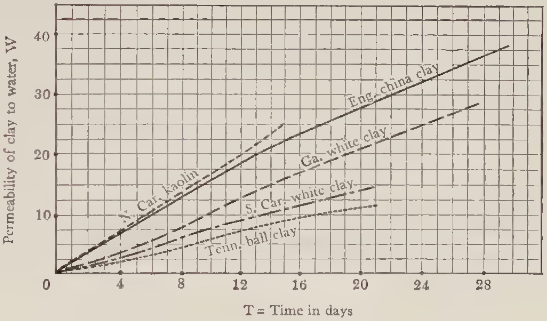

FIG. 83.

FIG. 82.—Apparatus for measuring the permeability of clays. (Schurecht, Jour. Amer. Ceram. Soc., V, 1922.)

FIG. 83.—Chart showing permeability of clays to water. (Schurecht, Jour. Amer. Ceram. Soc., V, 1922.)

It was found that the addition of sufficient NaOH increased the permeability in some clays tried. The author found that the permeability of clay to water is independent of time between two and ten days. Permeability is nearly constant in the formula $P = W/T$, in which W = total water passing through in T days. This factor P for North Carolina kaolin was 1.55 ±0.05; for English china-clay, 145 ±0.08. The permeability for Tennessee ball-clay was increased from 0.64 to 1.20 by adding 0.7 per cent NaOH.

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[1] H. G. Schurecht, Jour. Amer. Ceram. Soc., V, p. 928, 1922.

ADSORPTION

By this term is meant the power which a clay has of removing solid substances from solutions with which it is in contact.

More than fifty years ago T. Way[1] noticed that clays, and soils with a clay base, possessed extraordinary powers for absorbing water, but that in addition the clay substance exhibited greater facility for absorbing the bases contained in certain salts which were dissolved in water. This action was also selective, certain bases and substances being held so that they could not be washed out again.

Bourry[2] states that kaolins do not absorb more than 2 per cent of calcium carbonate from a solution, while plastic clays can absorb from 10 to 20 per cent of it. More recently Dr. Hirsch[3] has made a number of experiments to test the amount of dissolved salts which a clay can absorb when stirred up in a solution. He found that clays and kaolins absorb some of the dissolved salt, because after settling the supernatant liquid had a lower concentration than it did before; but sand and burned clay do not show this power, while feldspar and marble possess it to some extent. The amount of salt thus absorbed was independent of the time, and the removal of the salt ceased with the settling of the clay. It is, however, dependent on the kind of clay and kind of salt and the degree of concentration. Thus barium, lead, and aluminum compounds were removed in considerable quantities, while strontium, magnesium, and calcium salts were absorbed to a less degree. The acid of the salt seems to influence the result appreciably. Chlorides, nitrates, and acetates are absorbed more than sulphates, but alkali salts, except the carbonates, are not. The higher the concentration of the solution the greater the quantity of salt absorbed, although in a weak solution all of the salt may be carried down. The conditions are more complicated in the presence of several salts; thus the absorption of barium chloride is decreased by the presence of alkali salts, acids and bases, and entirely prevented by aluminum chloride. Sulphates are absorbed in the presence of caustic alkalies and acids, while the alkali chlorides seem to be lacking in effect.

Experiments by the author[4] have also shown that some tannins, as gallo-tannic acid, are absorbed by clay, a clear filtrate from a mixture of gallo-tannic acid and clay giving no reaction with ferric chloride.

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[1] Royal Ag. Soc. Jour., XI, 1880. Quoted by Cushman, Trans. Amer. Cer. Soc., VI, p. 7, 1904.

[2] Treatise on Ceramic Industries, p. 54, 1901.

[3] Tonindustrie-Zeitung, No. 26, 1904.

[4] Trans. Amer. Ceram. Soc., VI, p. 44, 1906.

In this connection it is of interest to refer to the observations of Kohler,[1] who finds that clays, among other substances, have the power of abstracting metallic oxides from solutions which are filtered through them.

E. C. Sullivan,[2] in experimenting along these lines, found that when a solution containing 100 c.c. of water with 252 grains of copper as the sulphate was shaken up with powdered orthoclase, albite, shale, or microcline, it was found that there was a remarkable interchange of bases instead of absorption. The copper entered the silicates, and an exact molecular equivalent of the K_2O, Na_2O, CaO, MgO, or MnO went into solution. The feldspar proved much more efficient than kaolin, and removed from 60 to 100 per cent of the copper from their liquid.

It has been pointed out that the mica content of a soil or clay is an important factor in adsorption, being responsible for 1 to 20 per cent of the total adsorption, as the content of mica varies from 2 to 37 per cent.[3]

Changes Taking Place in Firing

When clays are subjected to a rising temperature a number of changes of a physical or chemical nature may take place. These include: Loss of volatile constituents, vitrification, and changes in volume, color, porosity, hardness and specific gravity.

Any one of these changes may extend over a variable temperature range, which is not the same in all clays.

Loss of volatile constituents.—This includes the loss of chemically combined water by hydrous aluminum silicates, mica, hydrous iron oxides, hydrous aluminum oxides, and gypsum; the loss of sulphur by sulphides (especially iron sulphide) and gypsum, and of carbon dioxide by carbonates; the burning off of carbon. The loss of chemically combined water or dehydration is the most important of these processes, and it is due chiefly to the hydrous aluminum silicates present.

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[1] Adsorptionsprozesse als Faktoren der Lagerstättenbildung und Lithogenesis, Zeitschr. für prakt. Geologie, Feb., 1903, p. 49.

[2] The Chemistry of Ore Deposition, Jour. Amer. Chem. Soc., XXVII, p. 976, and Economic Geology, I, p. 67, 1905.

[3] Anderson, M. S., Fry, W. H., Gile, P. L., Middleton, H. E., and Robinson, W. O., U. S. Dept. Agric. Bull. 1122, 1922. For further references on adsorption of clays and clay minerals see: Patten, H. E., and Gallagher, F. E., U. S. Dept. Agric. Bull. 51, 1908; Ashley, H. E., U. S. Geol. Surv. Bull. 388, 1909; Gile, P. L., Middleton, H. E., Robinson, W. O., Fry, W. H., and Anderson, M. S., U. S. Dept. Agric. Bull. 1193, 1924.

Figure 84 shows the loss in weight of several clays due to driving off of volatile constituents.

Dehydration.—Considering all the minerals that may be involved, dehydration may begin as low as 150° C., and extend to probably 650° C., but most of it does not take place until a temperature of at least 450° C. is reached.

The change caused by loss of water may affect the plasticity, specific gravity, porosity, molecular arrangement and shrinkage of the clay, as well as its solubility in acids and alkalies.

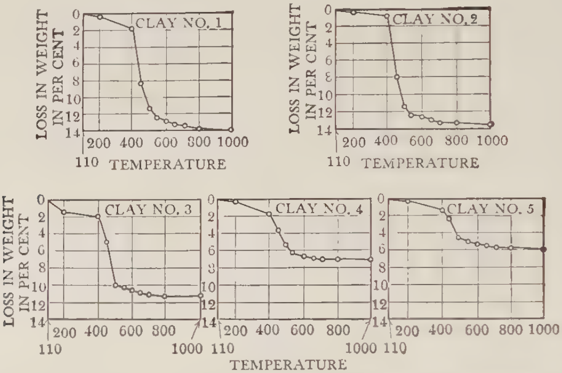

FIG. 84.—Loss in weight of several clays when heated to different temperatures. 1. N. Ca. kaolin; 2. Georgia sedimentary kaolin; 3. Tennessee ball clay; 4. Ohio fire clay; 5. Maryland fire clay. (Brown and Montgomery, U. S. Bur. Stand., Tech. Pap. 21, 1913.)

Hydrous aluminum silicates.—Much has been written regarding the dehydration temperature of clays, and various interpretations have been placed on it.

If we plot the temperature curve, it will be found that at those temperatures at which most of the combined water is driven off there will be a retardation, indicated by a terrace in the curve, and this represents an endothermic reaction. At a higher temperature the curve may exhibit what Mellor calls a hump due to exothermic reactions.

It is thought by some that these curves may be quite characteristic for certain clay minerals.[1]

Le Chatelier[2] was amongst the earliest observers of this property, and sought to show that the dehydration temperature varied from 150° to 770° C., depending on the hydrous aluminum silicates present.

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[1] Mellor, J. W., Trans. Ceram. Soc. (Eng.), XVI, p. 73, 1916–17.

[2] Zeit. physik. Chemie, I, p. 396, 1887; Compt. rend., CIV, p. 1443 and 1517; Dingl. polyt. Jour., CCLXV, p. 94, 1887.

Making use, therefore, of temperature dehydration curves, he recognized the following groups:

1. Halloysite: retardation between 150° and 200° C., again at 700° C., with sudden acceleration at 1000° C.

2. Allophane: retardation between 150° and 220°, and acceleration at 1000° C.

3. Kaolinite: retardation towards 770° C. and slight acceleration towards 1000° C.

4. Pyrophyllite: retardation at 700° C., and a second less distinct one at 850° C.

5. Montmorillonite: retardation at 200° C., a second at 770° C., and a third less marked one at 950° C.

Le Chatelier's curves seem open to some doubt, and his dehydration temperature of 770° C. for kaolinite is too high, according to later measurements.

As a rule the temperature curves of the purer clays seem to give better-marked halting points (Fig. 85), than those of the impure ones, and this fact seems to be well shown by curves published by Rieke,[1] and also by Brown and Montgomery.[2]

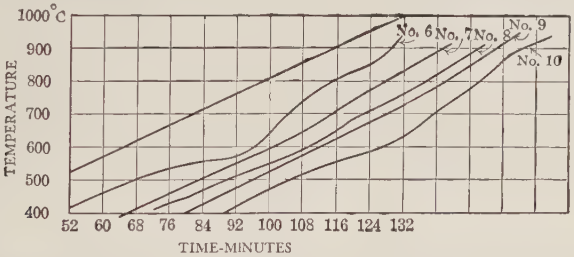

Fig. 85.—Dehydration curves of several clays. 6. Maryland flint clay; 7. Ohio shale; 8. Illinois shale; 9. Ohio surface clay; 10. Georgia surface clay. (Brown and Montgomery, U. S. Bur. Stand., Tech. Pap. 21, 1913.)

Many observers express the dehydration temperature as a range, rather than a single point. Some of the results obtained are as follows:

Lovejoy, 630° C., on a No. 2 fire-clay;[3] A. E. Barnes, 565° C.;[4] W. M. Kennedy, Florida "Kaolin," 475° C.;[5] Ashley, 500–575° C., and 825–925° C.;[6] Mellor and Holdcroft, most pronounced at 500°, but a lag between 600° and 700° C., with exothermic reaction at 900° C.;[1] Rieke, as low as 425°, but chief range between 510°–580° C.;[2] Brown and Montgomery, first lag between 450° and 520° C., but main lag between 480° and 670° C., depending on the clay.

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[1] Sprechsaal, XLIV, p. 637–641 and 653–656, 1911.

[2] U. S. Bur. Stand., Tech. Pap. 21, 1912.

[3] The Clayworker, 1888.

[4] Ibid., XXIII, p. 705, 1895.

[5] Trans. Amer. Ceram. Soc., IV, p. 152, 1902.

[6] Jour. Ind. and Chem. Eng., III, p. 91, 1910.

The following figures are given by Brown and Montgomery:[3]

Dehydration Temperatures of Several Clays

		I	II	III	IV
6	Maryland flint clay	450	550–575	10.45	870
7	Ohio shale	485	....	3.98	880
8	Illinois shale	480	–670	4.88	850
9	Ohio surface clay	....	no lag	5.63	
10	Georgia surface clay	490	600	10.09	

The purer clays gave more characteristic curves.

1	North Carolina kaolin	480	540–570	13.20	850
2	Georgia	525	525–590	12.93	850
3	Tennessee ball clay	510	510–600	10.67	
4	Ohio fire clay	520	550–600	6.69	Faint
5	Maryland fire clay	480	480–580	5.68	850–900 Faint

I. First lag.
II. Retardation.
III. Weight loss, 650° C.
IV. Exothermic reaction.

While a loss in weight may take place below 450° C., it is questionable whether it represents chemically combined water, but rather adsorbed moisture. Organic matter or water held by hydrous iron oxides may pass off at a low heat.

It has also been pointed out that the temperature range of dehydration may be due to a too-rapid rise of the temperature.

Thus Rieke mentions the case of a Bohemian kaolin that showed a loss of 4.11 per cent when heated for one hour between 470° C. and 475° C., while at the end of thirty hours at the same temperature it had lost 10.18 per cent. Another sample showed 8.42 per cent loss after two hours' heating between 510°–520° C., and 9.75 per cent at the end of twenty-one and one-half hours at the same temperature.

Houldsworth and Cobb[4] expressed the view that if kaolin were held long enough between 420°–450° C. that complete dehydration would occur.

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[1] Trans. Ceram. Soc. (Eng.), X, p. 94.

[2] Sprechsaal, XLIV, p. 637–641 and 653–656, 1911.

[3] U. S. Bur. of Stand., Tech. Pap. 21, 1912.

[4] Trans. Ceram. Soc. (Eng.), XXII, p. 111, 1922–23.

While somewhat in disagreement with this is the statement of Brown and Montgomery [1] that the combined water of clay is not expelled at any definite temperature, but leaves throughout a fairly long-continued temperature range, and furthermore that instead of dealing with pure hydrates, we have substances in which the water is held only in part as water of hydration. The acceleration at 850° C. appeared more distinct in the purer clays.

We therefore have two groups of views. One group considers that there is no loss of water at low temperatures.[2]

The other holds that there is no definite temperature at which water is evolved, and that the lower the temperature the slower the speed of dehydration.[3]

Some of these claim that even at atmospheric temperatures a loss of water may occur under favorable conditions.

The greatest loss, however, appears to occur between 500° and 600° C.

Bauxites do not seem to agree in their dehydration ranges with clays. Wohlin [4] notes three types, based on their heating curves as follows: (1) Diaspore type, dehydrating about 540° C., with 12–14 per cent loss; (2) Gibbsite type, dehydrating about 310° C., with 27–35 per cent loss; and (3) mixture of 1 and 2, losing part of water like (1) and part like (2), with ignition loss of about 20 per cent.

At about 1060° C. the alumina undergoes a more or less marked exothermal change accompanied by a reduction of volume.

These figures do not agree exactly with those given by Houldsworth and Cobb,[5] whose figures are diaspore, 370°–400° C.; gibbsite, 160°–190° C.; red bauxite, 350°–410° C.; gray bauxite, 200°–220° C., 390°–450° C. All show appreciable loss of water at the temperatures mentioned. Red bauxite is said to evolve appreciable heat at 1000° C.

Bleininger and Brown [6] noted that in plotting the heating curve of a clay in an electric furnace, the curve showed two distinct lags, one between 200° and 300° C., and another between 570° and 620° C. The first they regarded as due to expulsion of mechanical water, held very persistently, while the second, of course, was due to decomposition of the kaolinite molecule.[1]

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[1] U. S. Bur. Stan., Tech. Pap. 21, 1912.

[2] This has been stated by P. Schemjatschensky, Art. Naturf. Ges. St. Petersburg XXI, p. 281, 1796; A. Frenzel, Jour. prakt. Chem., V, p. 403, 1872; and A. Dick, Miner. Mag., VIII, p. 15, 1889.

[3] J. W. Mellor and A. D. Holdcroft, Trans. Eng. Ceram. Soc., X, p. 94, 1911; E. Löwenstein, Zeit. anorg. Chem., LXIII, p. 95, 1909; E. A. Wülfing, Jahres. Ver. Naturk. Wurttemberg, LVI, p. 1, 1900; R. Rieke, Sprechs., XLIV, p. 637, 1911; G. Keppeler, ibid., XLVI, p. 447, 1913; E. Manasse, Atti. Soc. Toscanna, XXVIII, p. 118, 1912; G. Tammann and W. Pape, Zeit. anorg. chem., CXXVII, p. 43, 1923.

[4] Sprechsall, XLVI, pp. 781–783, 1913; Silikat Ztg., I, p. 225–228. See also Kurnakow, N. S., and Urazov, G. G., Ann. Inst. Phys.-Chem. Anal. Leningrad II, p. 496, 1924.

[5] Trans. Eng. Ceram. Soc., XXIII, p. 279, 1923–24.

[6] U. S. Bur. Stand., Bull. 7, p. 29.

Change in Character of Dehydrated Material.—The clay which has been dehydrated may show a marked difference from the uncalcined material.

As pointed out by F. W. Clarke,[2] kaolin which has been dehydrated at low redness is completely decomposable by hydrochloric acid, but that the material contains no silica soluble in sodium-carbonate solution. This decomposition has been noted since by a number of other writers.[3] Sokoloff obtained the following results on heating the kaolin for five hours at different temperatures:

Temperature, ° C.	Loss on heating, per cent	Per cent of soluble Al_2O_3
400	3.85	
500	11.70	28.99
600	....	33.74
700	12.94	33.96
800	13.00	34.67

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[1] For further data on dehydration see: Bigot, A., Compt. rend., CLXXVI, p. 91, 1923; Bouduard, O., and La France, J., Bull. soc. chim., XXXIII, p. 1627, 1923; Bourry, E., Treatise on Ceramic Industries, p. 103; Houldsworth, M. S., and Cobb, J. V., Trans. Ceram. Soc. (Eng.), XXII, p. 111; Kennedy, W. M., Trans. Amer. Ceram. Soc., I; Keppler, G., Ber. der Tech. Wiss. Abt. des Verbds. ker. Gew. in Deutschland, 1913, p. 18; Laubman, Tonind.-Zeit., V, p. 400, 1881; Matijka, J., Chem. Listy, XVI, p. 8, 1922, and Min. abs., II, p. 131; Mühlhäuser, O., Tonind., Zeit., p. 149, 1881; Plenske, E., Sprechsaal, No. 21, p. 290, 1908; Rohland, Sprechsaal, 1905, p. 1745; Samoiloff, J. V., Trans. Ceram. Soc. (Eng.), XXIII, p. 338, 1923; Stremme, Sprechsaal, XLVII; Thomson, W., Jour. Soc. Dyers and Col., XXX, p. 45; Wallach, R., Compt. rend., CLVII, p. 48; Keppler, G., Sprechsaal. 1913, p. 447. For papers relating to dehydration of halloysite, see: Glinka, K., Studien in Gebiete der Verwitterungsprozresse, St. Petersburg, 1906, p. 1906, p. 57; Helmhacker, R., Tech. min. Mit., II, p. 229; Helmhacker, R., and John K. Neues Jahr. Min., 1879, p. 614. Le Chatelier, H., Bull. Soc. min., 1887, p. 204, and Zeit. fr. Phys. Chem., 1887, p. 396; Löwenstein, E., Zeit. anorg. Chem., LXIII, p. 95, 1909. For montmorillonite see Ross, C. S., and Shannon, E. V., Jour. Amer. Ceram. Soc., IX, p. 91, 1926. See also under Leverrierite.

[2] U. S. Geol. Surv., Bull. 125, p. 52.

[3] McNeil, Jour. Amer. Chem. Soc., XXVII, p. 590; Knote, Trans. Amer. Ceram. Soc., XII, p. 226, 1910; Mellor and Holdcroft, Trans. Ceram. Soc., Eng. X, p. 94; Sokoloff, Tonindus.-Zeit., XXXVI, p. 1107–1111; Iskiul, V. I., Ann. Inst. Anal. Phys.-Chim., Leningrad, II, p. 498, 1924.

There has been some disagreement as to the constitution of the material left after kaolinite is dehydrated, and no unanimity of opinion exists at present.

Knote [1] suggests the formation of $Al_2O_3 \cdot SiO_2$ and $Al_2O_3 \cdot 3SiO_2$.

Mellor and Scott claim that the kaolinite on dehydration just above 500° C. decomposes into free silica, alumina and water,[2] basing this conclusion on a comparison of the dehydrated clay with artificially prepared alumina, and finding close similarity in regard to variation in specific gravity, hygroscopicity, solubility in acids, and exothermic change indicated by the heating curve around 900° C.

J. V. Samoiloff [3] advanced a still different view, viz.: that the kaolinite is decomposed into two different compounds, Al_2SiO_5 and SiO_2.

G. Shearer points out that the X-ray pictures of the dehydrated kaolinite show absence of crystalline structure, except where pieces of undecomposed kaolinite remain.[4]

Even the change at 900° C. is not explained by all observers in the same manner.

Knote believes that there is a recombination of the SiO_2 and Al_2O_3, while Mellor called it polymerization of the Al_2O_3 and Ashley suggested the formation of sillimanite.

F. W. Clarke [5] and W. Vernadsky [6] assume that the anhydride, $Al_2Si_2O_7$, which they call leverrierite is formed.

Vernadsky in his earlier paper suggested that at 900° C. the leverrierite went by polymorphic and slow changes into free silica and sillimanite while in a later paper [7] he states that above 1000° C. the leverrierite changes to cristobalite and mullite or keramite.

Samoiloff disagrees with Vernadsky in thinking that at 900° C. there is a molecular rearrangement of Al_2SiO_5.

Mellor and Scott [8] explain the change by saying that the amorphous alumina passes to the crystalline form.

K. A. Vesterberg [9] claims that the kaolinite at 800° C. forms

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[1] Trans. Amer. Ceram. Soc., XII, p. 226, 1910.

[2] Trans. Ceram. Soc., (Eng.), XXIII, p. 322, 1923–24.

[3] Trans. Ceram. Soc. (Eng.), XXIII, p. 339, 1923–24, and Bull. de l'acad. des Sciences de la Russie, 1909, p. 1137.

[4] Trans. Ceram. Soc. (Eng.), XXII, p. 106, 1923.

[5] U. S. Geol. Surv., Bull. 125, p. 32, 1875.

[6] Trans. Ceram. Soc. (Eng.), XXII, pp. 398–401, 1922–3.

[7] Ibid., XXIV, p. 13, 1925.

[8] Trans. Ceram. Soc. (Eng.), XXIII, p. 326, 1923–24.

[9] Arkiv. Kemi. Min. Geol., IX, No. 14, 1–26, 1925.

$Al_2Si_2O_7$, which is sol in HCl. Pyrophyllite, he says, is not rendered soluble by heating.[1]

If kaolinite is examined with the microscope, it appears optically homogeneous when heated up to 1200° C.[2] but dissociation appears to begin above this point, and as the temperature is raised the dissociation increases very slowly at first, and then at an increasing rate, until at 1400° C. it seems to be complete. The products of dissociation are said to be silica and amorphous aluminum silicate. At about 1450° C. the amorphous aluminum silicate changes into crystalline "sillimanite." R. E. Somers[3] differs from Klein in finding that in clays fired at 1150°C. the hydromica became isotropic, but the kaolinite did not.

It is possible that the difference may have been due to Klein's samples having been fired more slowly.

The dehydration is an endothermic process absorbing, according to Navias,[4] 240 calories per gram under assumption that steam is condensed to liquid at room temperature.

The clay in its dehydrated form has its highest porosity and remains very porous until about 900° C.

Rehydration.—Clays which have been almost completely dehydrated by calcination at a moderate temperature (600°–700° C.) can be rehydrated by heating with water to 200°–270° C. for eight to forty-eight hours.[5] The rehydrated material is usually plastic and appears to be colloidal. They argue from this that the kaolinite on dehydration appears to form an anhydride, which is broken down by heating to higher temperatures.

Washburn considers that there is no doubt that the burned clay slowly rehydrates in contact with water, but that the rate is influenced by the time, temperature, nature and condition of the body.[6]

Dried clays.—It has been found that if finely powdered samples of clay are dried over 25 per cent H_2SO_4, and then placed in desiccators containing H_2SO_4 of different concentrations up to 90 per cent, with the temperature held at 25° C. that all showed a loss of water, but that this might be gradually resorbed on exposure to a moist atmosphere.[7]

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[1] For further references see O. Boudouard and J. Le France, Bull. soc. chim., XXIII, p. 1627, 1925; C. E. Moore, Trans. Ceram. Soc. (Eng.), XXII, p. 138–58, 1922–3.

[2] Klein, A. A., U. S. Bur. Stand., Tech. Pap. No. 80, p. 35; also Trans. Amer. Cerem. Soc., XVIII, p. 377, 1916.

[3] U. S. Geol. Surv., Bull. 708, p. 305, 1922.

[4] J. Am. Ceram. Soc., VI, 1268.

[5] Laird, J. S., and Geiler, R. F., Jour. Amer. Ceram. Soc., II, p. 828, 1919.

[6] Jour. Amer. Ceram, Soc., IV, 1921.

[7] Mellor, Sinclair and Devereux, Trans. Ceram. Soc. (Eng.), XXI, p. 104–6, 1921–22.

Figures for a few clays are given below:

PERCENTAGE OF LOSS IN WEIGHT OF DIFFERENT CLAYS IN DRIED ATMOSPHERE ON EXPOSURE TO SULPHURIC ACID *

Per cent of H_2SO_4	Halloysite	Ball clay	China clay
30	1.72	0.08	0.16
40	8.68	0.24	0.12
50	10.36	1.63	0.20
60	11.40	2.31	0.24
70	11.52	2.44	0.46
80	12.52	3.29	0.52
90	11.84	3.54	0.55

* The exposure was three months.

Hydrated ferric oxides.—Posnjak and Merwin [1] have plotted dehydration curves for goethite ($Fe_2O_3 \cdot H_2O$), lepidocrocite and limonite, all of which show clearly what part of the water was chemically combined and what part absorbed. The curves all have a sharp drop somewhere between 150° C. and a little over 200° C. The exact temperature at which the combined water goes off could not be determined but it is somewhere between these limits. The differences, if any, between the dehydration temperatures of the goethite, lepidocrocite and limonite, are quite similar. The mineral would take up nearly as much absorbed water as it had at first if exposed to air after dehydration. In one of the limonites 3 per cent of adsorbed water was still retained at 300° C. while in the goethite it was 1 per cent or less. Turgite has a smooth dehydration curve showing continuous loss of water with rising temperature thus indicating that there is no decomposition of a definite chemical compound.

Gypsum.—This mineral will lose its chemically combined water at a rather low temperature, probably mostly between 120° C. and 200° C. (see Gypsum).

Carbon and carbon dioxide.—Both of these constituents will be driven off mostly between 800° C. and 900° C., but may in part at least pass off earlier.

Sulphur oxides.—These may come either from pyrite or gypsum. The former may yield its sulphur at as low a temperature as 560° C., but the latter does not become dissociated until a temperature of about 1000° C. is reached.

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[1] Amer. Jour. Sci. (4), XLVII, pp. 311–348, 1919.

Oxidation period.—This term may be applied to that period in the firing when certain changes take place which require oxygen for their accomplishment. This may include the burning off of combustible matter such as carbon or hydrocarbons, the expulsion of sulphur, and the change of iron from the ferrous to the ferric condition.

Oxidation may begin at a comparatively low temperature, and is probably completed by 900° C. Since, however, there may be at times considerable material in the clay requiring oxidation, and the clay may be rather dense thus preventing easy access of air to the interior of the piece, it is occasionally necessary to hold the clay for some time below 900° C. until oxidation is completed. (See under Carbon.)

Loss of volatile products in burning.—The analyses (see table below) giving the composition of several clays, and the bricks made from them, are interesting in showing the loss of the volatile products in burning.

Analyses Showing Difference between Raw and Burned Clay *

	I	II	III	IV	V	VI	VII
Silica (SiO_2)	74.03	78.5	74.04	73.94	49.45	56.6	56.5
Alumina (Al_2O_3)	17.10	21.3	15.15	20.47	17.11	20.4	20.2
Ferric oxide (Fe_2O_3)	.57	Tr.	.50	1.80	3.45	6.2	6.1
Lime (CaO)	.10	....	.50	1.08	12.67	11.7	11.6
Magnesia (MgO)	.22	....	.27	1.16	1.77	1.4	1.8
Potash (K_2O)	.30	.5	.42	.61	.13	1.5	1.5
Soda (Na_2O)	.60	.3	1.12	.64	.21	1.4	1.3
Titanium oxide (TiO_2)	1.36	With Al_2O_3	1.31	.83	.70	With Al_2O_3	With Al_2O_3
Water (H_2O)	6.15	None	6.00	....	4.84	.5	None
Carbon dioxide (CO_2)	....	....	....	....	7.10	None	None
Sulphur trioxide (SO_3)	....	....	....	....	2.00	None	None
Ferrous oxide	....	....	....	....	....	None	None
Total	100.43	100.6	99.31	100.53	99.43	99.7	99.1

I. Fire-clay from six miles southeast of Sulphur Springs, Tex. O. H. Palm, analyst.
II. Brick from same. S. H. Worrell, analyst.
III. Fire-clay, Athens, Tex. O. H. Palm, analyst.
IV. Fire-brick, Athens, Tex. O. H. Palm, analyst
V. Brick shale, Ferris, Tex. O. H. Palm, analyst.
VI. Brick from same. O. H. Palm, analyst.
VII. Hard-burned brick from V. O. H. Palm, analyst.

* These analyses would have been of greater value had it been possible to make each of a pair on the same sample. The main point they bring out is the loss of volatile elements.

Change in color.—As pointed out under iron oxide, this is the common coloring agent in fired clays, and the facts given there need not be

repeated here. Lime carbonate when in excess over iron oxide, and both evenly distributed will yield a cream-colored brick. Even titanium may probably exert a slight coloring action on some iron-free clays, although present in only small amounts.

Of considerable importance is the condition of the fire whether oxidizing or reducing, the former giving bright colors.

Firing under oxidizing conditions in a muffle usually gives brighter color than in an open kiln where flames come in contact with the ware.

Much reoxidation may, however, take place during cooling in a large kiln.

The rapid cooling of a small kiln does not cause much difference in the color of fired clays, which have been fired under oxidizing conditions.

Wilson [1] states that the following changes in color will be produced when test-pieces are subjected to reducing conditions produced by direct contact with flame or combustion gases (open firing), or through thin-walled and porous saggers, and when not followed by long oxidizing cooling period above red heat after the firing is stopped:

1. White and light creams will change to white having a blue or grayish tone, deepening into light grays.
2. Bright buffs will fade to grays and brown grays.
3. Bright reds will change to red browns and blacks.
4. Black iron spots become more prominent in all the above colors.

Clays of high iron content show the greatest difference.

VITRIFICATION

Immediately after a clay has been dehydrated it shows its maximum porosity, as, however, the temperature is raised, some of the clay particles begin to soften by fusion, binding the mass together.

As the temperature continues to rise, more of the mass becomes softened, and more of the clay body goes into solution so that the composition of the softened portion changes.

It will be seen, therefore, that while in the early stages of vitrification, there may be considerable pore space between the grains, these will be gradually filled by fused material, provided there is a sufficient quantity of it.

We may recognize three stages in the vitrification process as follows: 1. Incipient vitrification, in which just enough of the clay material has softened to stick the mass together. 2. Complete vitrification, at which point the interspaces are filled with fused material, the mass, however, being still able to support its own weight without distortion. 3. Fusion at which point the body has softened so that it no longer holds its own weight.

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[1] Univ. Wash. Eng. Exper. Sta., Bull. 18, p. 32, 1923; see also p. 259.

Incipient vitrification begins at different temperatures in different clays.

According to Searle it may begin in some very fusible clays as low as 450° C. In most clays it probably does not begin below 750° C. or 800° C.

Searle[1] defines the vitrification range as the "range of temperature between the commencement of fusion and the loss of shape due to the production of vitrified material."

Coincident with the vitrification process, there takes place a diminution in volume, and also change in porosity.

The volume change, or shrinkage, increases until the clay is completely vitrified, after which it decreases, due to the clay swelling.

It has been noted however that different clays after reaching complete vitrification may remain in that condition over a rather long temperature interval, before swelling or overfiring begins. They have a long firing range. With others the reverse is true.

Aside from this, however, the temperature interval between incipient vitrification, vitrification and fusion may vary considerably.

Wheeler[2] gives the following temperature ranges for several classes of clays, between incipient vitrification and scoriaceous vitrification The figures are based on 135 clays tested.

Number	Percentage	Range		Character
		° F.	° C.	
2	1.5	75	24	Very calcareous
33	24.5	300	149	Very impure clays and shales
11	8.0	350	176	Less impure clays and shales
63	47.0	400	204	Fire clays, potters clays, kaolins
26	19.0	500	260	Some china-clays, pure fireclays
135	100.0			

Mathews[3] tabulates 220 clays according to their firing range, and divides them into two groups as follows:

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[1] Chemistry and Physics of Clays, p. 552.

[2] Mo. Geol. Surv., XI, p. 131, 1896.

[3] Md. Geol. Surv., XI, Pt. II, p. 50, 1922.

I. "In this group 190 show a range from incipient vitrification to viscosity of less, and thirty of more than 278° C. Of these only forty-three show greater temperature range between vitrification range and viscosity, than between incipient and complete vitrification." II. "In the second group, where the total range is between 278° C. and 500° C., nearly 75 per cent show wider ranges from complete vitrification to fusion."

He adds: "From the figures obtained it is evident that most of the clays of low gross range allow relatively less range in temperature above that of complete vitrification or optimum density than do those clays with a gross range of more than 278° C., which also show a greater latitude in temperature before reaching viscosity."

"There is no striking relationship shown between clays of low incipient fusion and low range to viscosity beyond the fact that those showing incipient vitrification below 1090° C. seldom show over 195° C. gross range from incipient vitrification to viscosity. Clays more refractory than this may show wide differences in range and in a general way the highly refractory clays pass quickly from incipient to complete vitrification."

We can thus say that the point of complete vitrification may lie midway between incipient vitrification and viscosity, or near to one or the other end-points of the range.

It is of course difficult to definitely decide the three points in the vitrification range, because there is usually a gradual change from one stage to the next.

There is a practical importance in the position of the complete vitrification point, for two reasons. Some wares have to be fired to a condition of minimum porosity, or vitrification as it is commonly called.[1]

Since the temperature of a kiln cannot be controlled very closely, it is desirable that there should be a sufficiently large temperature interval between complete and viscous vitrification, in order to avoid the risk of overstepping one and passing into the other. This explains why calcareous clays, for example, are not adapted to the manufacture of vitrified ware.

The other point is that a clay which can be vitrified at a lower temperature, will require less fuel in firing than one which has a high temperature of vitrification.

Bleininger and Loomis [2] present a number of interesting curves of refractory bond clays. They remark "that in general it may be said that the longer the temperature interval between the point of greatest density (lowest porosity) and the temperature of overburning—and likewise the higher the temperature at which overfiring occurs—the more useful should be the clay as a refractory material."

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[1] Orton has pointed out that the term vitrified, signifies a condition of glass, and that if the ware were thoroughly vitrified it would be extremely brittle. In actual practice therefore the process of firing does not reach this point completely.

[2] Trans. Amer. Ceram. Soc., XIX, p. 601, 1917.

Porosity and vitrification.—While the clay is highly porous after dehydration, and the pores open and connecting, it is quite evident that when vitrification begins the channels connecting some of the pores become closed. We thus have developed two types of pores, open and closed.

The method for determining the volume of both types of pores has already been referred to (see Porosity).

Since gases may be evolved from the clay as vitrification progresses, if it is released in the closed pores, these may become enlarged by the expansive force of the gases, especially if the viscosity of the clay is considerable.

Indeed the evolution of gases during firing may be responsible for the porosity, especially if this is rapid enough.

The gases evolved may include [1] combined water, carbon dioxide resulting from the combustion of carbon and dissociation of carbonates, sulphur dioxide and trioxide from pyrite or gypsum, and oxygen from the reduction of ferric oxide.

As vitrification is a very important character in the manufacture of dense products such as paving-brick, sewer-pipe, stoneware, porcelain, etc., its manner of progression, and development of vesicular structure need to be carefully considered, for the overdevelopment of porosity may cause serious harm.

Bleininger and Montgomery [2] group clays as follows as regards the structure developed:

1. Open structure, no vitrification possible. (Pure clays, kaolins, flint clays, very siliceous clays.)
2. Sound vitrification, with no immediate development of vesicular structure (Fig. 87). (Best paving-brick shales, stoneware clays and similar ones.)
3. Vesicular structure, developed before vitrification. Sound vitrification impossible. (Many shales which fail to make satisfactory paving-blocks.)
4. Vesicular structure, developed coincident with or immediately after vitrification. (Those showing such short firing range (Fig. 86) as to interfere with proper firing under commercial conditions.)

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[1] Bleininger and Montgomery, U. S. Bur. Stand., Tech. Pap. 22.

[2] U. S. Bur. Stand., Tech. Pap. 22, 1913.

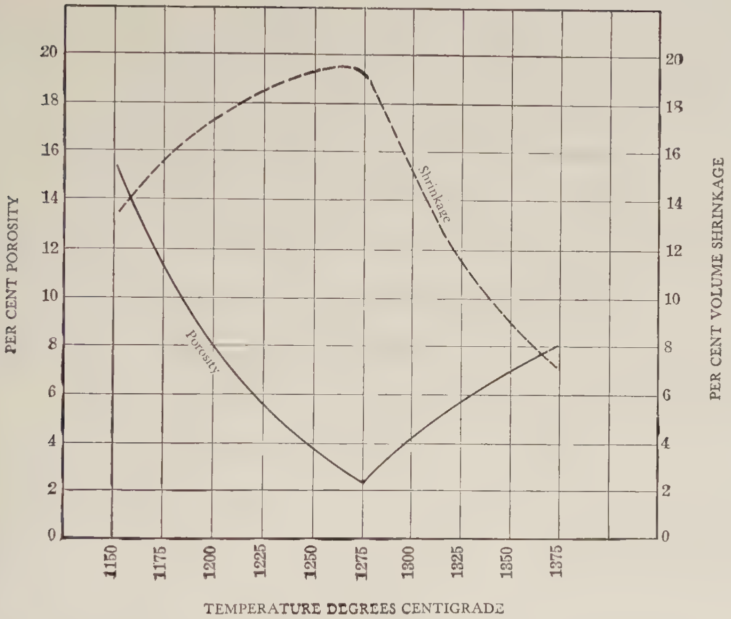

FIG. 86.—Clay with short firing range. (Brown, Jour. Amer. Ceram. Soc., I, 1918.)

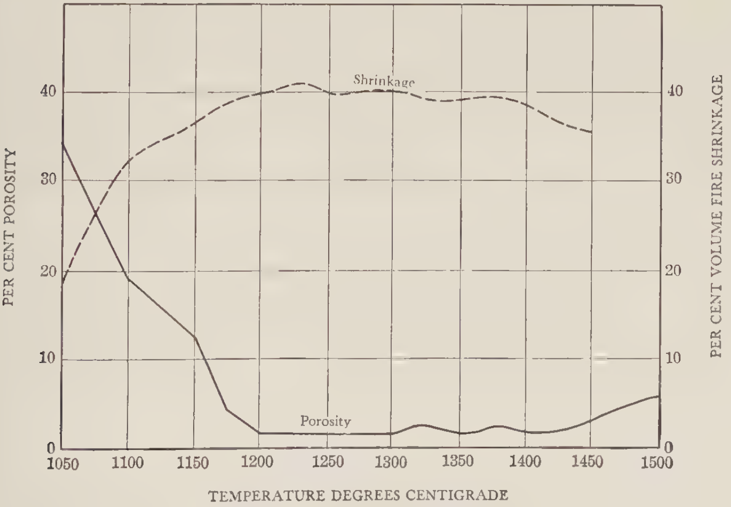

FIG. 87.—Clay with long firing range, a Tennessee ball clay. (Bleininger and Loomis, Trans. Amer. Ceram. Soc., XIX, 1917.)

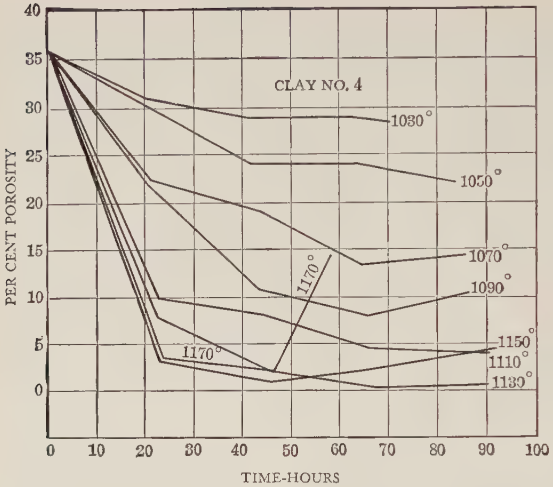

FIG. 88.—Chart showing relation between time and porosity in firing a red burning Ohio surface clay. The 1150° and 1170° curves show overburning. (Brown and Murray, U. S. Bur. Stand., Tech. Pap. 17, 1913.)

Brown and Murray state that a vesicular structure may be produced not only by excessive temperature, but also by longer-continued burning at lower temperature.[1]

Effect of time on vitrification.—It is a well-recognized fact that in general, time is an important factor in vitrification. In other words exposing a clay to a lower temperature for a longer time produces as much vitrification, as exposing it to a higher temperature for a shorter time.

Some clays are naturally more affected than others, the results being more pronounced in those clays with slower acting fluxes.

Figure 89 from Brown and Murray [1] shows the effect of time on vitrification.

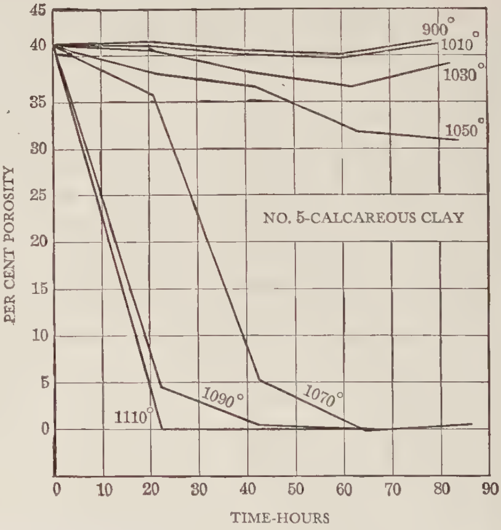

FIG. 89.—Chart showing function of time in vitrification of a calcareous clay. (Brown and Murray, U. S. Bur. Stand., Tech. Pap. 17, 1913.)

Bleininger and Boys [2] showed that in the case of a certain shale, 10 per cent porosity was reached after heating seventy-two minutes at a constant rate up to 1200° C. and in 536 minutes at a temperature of 1150° C. The rates of heating were 16.6° C. and 2.1° C. per minute, respectively.

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[1] Trans. Amer. Ceram. Soc., XIII, p. 392. See also Brown and Murray, Bur. Stand., Tech. Pap. 17, 1913.

[2] Trans. Amer. Ceram. Soc., XIII, p. 387.

Brown and Murray also note[1] that rapid firing requires a higher finishing temperature than slower firing.

Vesicular structure is produced not only by excessive temperature, but also by longer-continued heating at a lower temperature, and the greater the tendency of a clay to produce vesicular structure the lower should be the firing temperature with a corresponding increase of time.

They also state from a study of a series of clays, that while no general rule governing time-temperature relations can be worked out, the higher the flux content, the more marked the influence of the time factor.

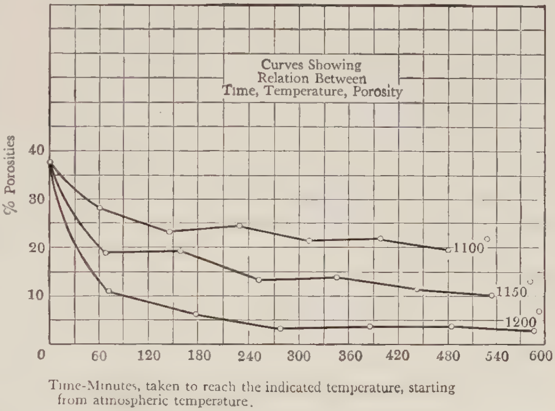

Fig. 90.—Curves illustrating effect of time upon vitrification as determined by porosity changes. (Beecher, Ia. State Coll. Agr., XIV, 1915.)

Shrinkage and vitrification.—As vitrification proceeds, the clay shrinks so far as its exterior volume is concerned, although there may be an actual increase in volume due to more and more of the clay material entering into fusion. This increase in the amount of fluid material tends to draw the unfused particles into closer contact, thus filling the pores, while the mass contracts.[2]

A point is finally reached when shrinkage ceases and swelling begins. This swelling may be due in part to the amount of material involved in the fusion process and in part to the formation of vesicles caused by the expansion of escaping gases. As pointed out by Bleininger, " the rate of contraction is not merely proportional to the temperature, but it is also a function of the viscosity at any given point. If at any stage the viscosity has been lowered the contraction will take place more rapidly per unit of temperature increase, than when the mass possesses a higher degree of molecular cohesion." It may, therefore, happen that the rate of contraction is greater at lower than higher cones.[1]

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[1] U. S. Bur. Stand., Tech. Pap. 17, 1913.

[2] Attention has been called to the fact under Fire Shrinkage, that some clays may expand slightly at temperatures below 1000° C. Much of this may be due to the inversion of α — β quartz, which takes place between 500–600° C. R. F. Geller and R. A. Heindel (Jour. Amer. Ceram. Soc., IX, p. 563, 1926) noted this in about half of a large number of sagger clays investigated by them.

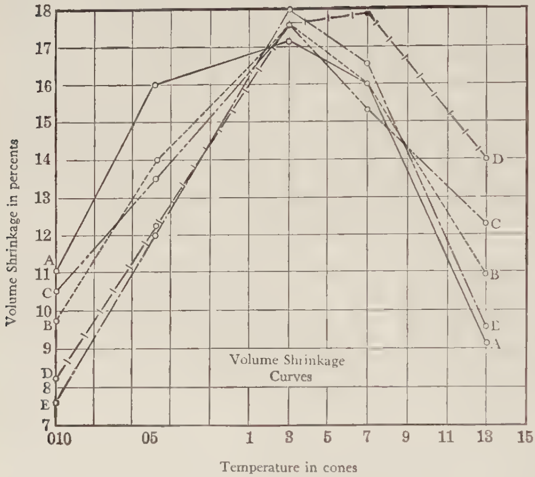

FIG. 91.—Curves showing volume changes of fire clays during burning. Pores decrease with decreased volume, and increase on overfiring. (Beecher, Ia. State Coll. Eng. Exper. Sta. Bull. 40, 1915.)

In burning clay products conditions of equilibrium are never reached,[2] and if a piece of fired ware is reheated to the same temperature as before, it may show further shrinkage. However, the higher the temperature, the less the additional contraction on refiring.

Specific gravity and vitrification.—In general there seems to be a decrease in true and apparent specific gravity as vitrification proceeds, but there may be exceptions.[3] This is discussed in more detail under specific gravity.

Development of minerals.—In the firing of clays, the reactions taking place in the fused material may result in the formation of new minerals, which can often be optically identified.

Among those the most frequently noted are certain needle-like forms, which investigators have described in many ceramic wares, and which when studied under the microscope, have commonly been identified as sillimanite.[4]

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[1] Bleininger and Stull, Trans. Amer. Ceram. Soc., XII, p. 629.

[2] Bleininger and Brown, loc. cit., p. 42.

[3] Bleininger and Montgomery, Trans. Amer. Ceram. Soc., XV, p. 79; Beyer and Williams, Ia. Geol. Surv., XIV, p. 116; Beecher, Ia. State Coll. Eng. Exper. Sta., Bull. 40, 1915; Schurecht, Md. Geol. Surv., XI, Pt. II, 1922.

[4] Ehrenberg, C. G., Pogg. Ann., XXXIX, p. 101, 1836; Oschatz, A., and Wächter, A., Ding. Poly. Jour., CVI, p. 322, 1847; Behrens, H., Pogg. Ann., CL, p. 386, 1873; Hussak, E., Sprechs,, XXII, p. 153, 1889; Vernadsky, W., Bull. Soc. Min., Fr., XIII, p. 256, 1890; Mellor, J. W., Jour. Soc. Chem. Ind., XXVI, p. 375, 1907;

Bowen and Greig[1] state, however, that the crystals which have been called sillimanite all have the composition $3Al_2O_3 \cdot 2SiO_2$, a mineral which they term *mullite.*

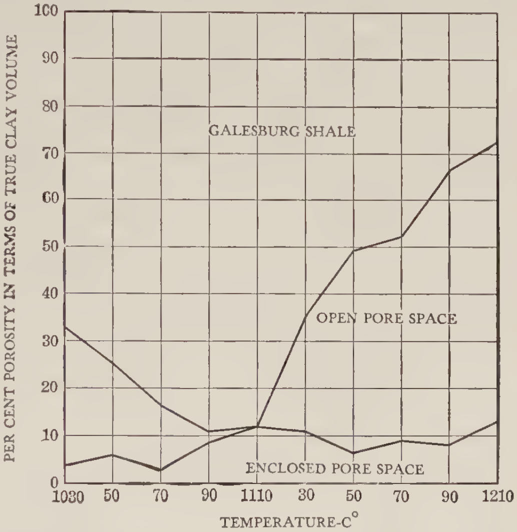

Fig. 92.—Pores in Galesburg, Ill., shale fired at different temperatures. (Bleininger and Montgomery, U. S. Bur. Stand., Tech. Pap. 22, 1913.)

The compound $Al_2O_3 \cdot SiO_2$, which occurs as sillimanite, andalusite, and cyanite has been regarded as the only compound of silica and alumina occurring in nature.

Sillimanite was regarded as the stable one under pyrogenetic conditions.

"Investigation of equilibrium relations of alumina and silica has shown that there is only one compound of these oxides stable in contact with liquid in the binary system. This compound is $3Al_2O_3 \cdot 2SiO_2$, but crystals of it show such remarkable similarity with natural sillimanite that they have been identified with it by a

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Trans. Eng. Ceram. Soc., V, p. 75, 1906; Heath, A., and Mellor, J. W., Trans. Ceram. Soc. (Eng.), VII, p. 80, 1908; Plenske, E., Sprechs., XLI, p. 256, 1908; Glasenapp, M., Tonindus.-Zeit., XXXI, p. 1167, 1907; Watts, A. S., Trans. Amer. Ceram. Soc., XI, p. 185, 1909; Klein, A. A., ibid., XVIII, p. 377, 1916; Ries, H., and Oinouye, Y., Trans. Amer. Inst. Min. Engrs., LVIII, p. 184, 1917; Wegemann, C. H., Trans. Amer. Ceram. Soc., IX, p. 231, 1907; Peck, A. B., Jour. Amer. Ceram. Soc., II, p. 175, 1919; Wilson, G. V., Jour. Soc. Glass. Tech., II, p. 177, 1918; Shepherd, E. S., and Rankin, G. A., Amer. Jour. Sci. (4), XXVIII, p. 301, 1919; Wallace, R. C., Zeit. anorg. Chem., LXVIII, p. 370, 1910; Cronshaw, H. B., A microscopic study of bone china body, Eng. Ceram. Soc., XVII, Pt. I, p. 151, 1917; Klein, A. A., Jour. Amer. Ceram. Soc., III, p. 978, 1920; Kondo, S., Microscopic structure of common brick, Jour. Jap. Ceram. Assoc., 370, p. 238–91, 1923; Bigot, A., Compt. rend., CLXXVIII, p. 569, 1924; Kempcke. E., Keramos, III, p. 551, 1924; Eitel, W., Keram. Rundschau, XXIII, p. 470, 1924; Raaz, F., Mineralog. petrog. mitt., XXXVIII, p. 583, 1925; Cousen, A., and Turner, W. E. S., Jour. Soc. Glass. Technol., 1925, p. 334; Houldsworth, H. S., Trans. Ceram. Soc. (Eng.), XXIV, p. 33, 1925; Harrison, H. C., and McCaughey, W. J. Jour., Amer. Ceram. Soc., IX, pp. 257 and 271, 1926.

[1] Jour. Amer. Ceram. Soc., VII, p. 250, 1924.

number of workers examining synthetic mixtures and artificial products of various kinds."

The authors investigation showed that the 3 : 2 compound is the only stable one at both high temperatures and at those as low as 1000° C. and probably much lower.

They have identified it in sillimanite buchites from Mull in Scotland,[1] hence the name Mullite which they have proposed.

Sillimanite they state " does not form in any alumina-silica mixture at any temperature at which the crystals grow to a sufficient size to be determinable." The addition of fluxes to alumina-silica mixtures to lower the fusion-point, gave crystals at 1050° C. but these were always $3Al_2O_3 \cdot 2SiO_2$.

Mullite was synthesized by Sainte Claire Deville and Caron [2] in 1865. Vernadsky separated crystals of it from Sévres porcelain in 1890, but assigned to them a formula $11Al_2O_3 \cdot 8SiO_2$ and Cox separated crystals of the material from burned fire-clay. [3]

The analysis of the material given by the several preceding authors make the composition as slightly more siliceous than the 3 : 2 ratio, but not so siliceous as the 11 : 8 ratio, and they agree rather closely with Mullite.

Analyses of Mullites

	I	II	III	IV	V	VI	VII
SiO_2	29.1	29.7	30.07	28.89	29.36	29.04	28.2
Al_2O_3	70.9	70.3	69.93	71.11	69.05	69.63	71.8
Fe_2O_3	....	....	....	....	.86	.50	
TiO_2	....	....	....	....	1.12	.79	
MgO	....	....	....	....	0.10	NaO K_2O .24	
	100.00	100.00	100.00	100.00	100.49	100.49	100.00

I. Artificial Mullite prepared by Deville.
II. Artificial Mullite prepared by Vernadsky.
III. } Artificial Mullite prepared by Cox.
IV.
V. Mullite from crowns of glass pots. Bowen, analyst.
VI. Mullite from Seabank Villa, Island of Mull. (Contained .51 per cent corundum and .1 per cent rutile which were determined separately.) Zies, analyst.
VII. Theoretical composition $3Al_2O_3 \cdot 2SiO_2$.

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[1] For description see Quart. Jour. Geol. Soc., LXVIII, p. 229, 1922; and Geol. Surv. Scotland, Mull sheet 44, 3rd ed., 1923.

[2] Ann. Chim. Phys., V. p. 114, 1865.

[3] Geol. Mag. (6), V, p. 61, 1918.

They express the belief that the X-ray spectrum cannot be used for distinguishing between sillimanite and mullite.

The optical and crystallographic properties of the two are said to be similar.

Mullite breaks up at 1810° C. into corundum and liquid.

The interesting point is also brought out that the most refractory mixture of alumina and silica is not the 1 : 1 mixture as usually thought, for it begins to melt at 1545° C. The $3Al_2O_3 \cdot 2SiO_2$ is more refractory melting at 1810° C.

In the presence of Fe_2O_3 and TiO_2, mullite may take these oxides into solid solution, changing its properties to resemble sillimanite.

The properties of mullite and sillimanite as given by Bowen, Greig and Zies [1] are as follows:

		Mullite Orthorhombic	Sillimanite Orthohombic
Prism angle...($110 \wedge 1\bar{1}0$)		89° 13′	88° 15′
Cleavage...............		‖010	‖010
Optical orientation....		$c = \gamma$	$c = \gamma$
		$b = \alpha$	$b = \alpha$
Refractive indices....	γ	1.654	1.677
	α	1.642	1.657
Axial angle..........$2V$		+ 45°–50°	+ 25°

	Sillimanite	Mullite
SiO_2..................	37.08	27.60
Al_2O_3..................	63.11	73.16
Fe_2O_3..................	.09	Tr.

While Bowen and Greig,[2] Shearer,[3] and Norton [4] were apparently unable to notice a difference in the diffraction patterns of sillimanite and mullite, Navias and Davey,[5] point out certain differences which they have found in the lines of the spectra.

J. W. Greig [6] found that cyanite, andalusite and sillimanite are all

[1] Jour. Wash. Acad. Sci., XIV, p. 183, 1924.

[2] Jour. Amer. Ceram. Soc., VII, p. 238, 1924.

[3] Trans. Ceram. Soc. (Eng.), XXII, p. 105, 1922–23.

[4] Jour. Amer. Ceram. Soc., VIII, p. 401, 1925.

[5] Jour. Amer. Ceram. Soc., VIII, p. 640, 1925; ibid., VIII, p. 296, 1925.

[6] Jour. Amer. Ceram. Soc., VIII, p. 465, 1925.

decomposed on heating, to mullite and silica or to mullite and siliceous liquid. The silica he believes is probably cristobalite. The decomposition temperature is not sharply defined, but the rate of decomposition increases rapidly with rise in temperature. Since the mullite has a lower density than the original minerals the change involves an expansion.

Mellor and Scott,[1] after a study of the action of heat on kaolinite, came to the conclusion that sillimanite of the same composition as the natural mineral " can develop at temperatures below 1200° C. and probably above that temperature forms solid solutions with $3Al_2O_3 \cdot 2SiO_2$. A new compound is formed when kaolinite is heated to 1700° C. This may be $3Al_2O_3 \cdot 2SiO_2$," and for this they suggest the name *Keramite.* They state in a footnote that since their paper was written it has been described by Bowen and Greig as *mullite.*

G. V. Wilson,[2] from a study of glass refractories found the development of corundum and " sillimanite " usual, with feldspar, magnetite and biotite occasional.

The white, porcelain-like layers of pots and bricks are, he states, often packed with minute needles of " sillimanite, but siliceous clays practically never." [3]

The formation of hematite has been noted by Belliere, who says that lamellar crystals of it were formed at the mouth of a covered porcelain crucible which had been in a pottery furnace during one burning.[4]

S. Kondo,[5] in describing the petrography of a number of bricks fired at cone 09 — 05, notes the presence of considerable amounts of " sillimanite."

Fluxing and resorption.—Klein [6] found that in quartz–feldspar mixtures fired up to 1340° C. the quartz dissolves only to a small extent in the feldspar glass, but that at 1460° C. the quartz is practically completely dissolved in mixtures having as much as 50 per cent quartz content.

At 1340° C., the kaolinite of a kaolin-feldspar mixture dissociates entirely, and what he calls amorphous and crystallized sillimanite increases with an increased content of kaolin. At 1460° C., 10 per cent kaolin appears to be entirely soluble in feldspar glass. At 1310° C., in quartz-clay-feldspar bodies the feldspar is a glass, with the clay almost completely dissociated, with the formation mainly of amorphous with little crystallized sillimanite, while the quartz is undissolved, but at 1380°–1400° C. the feldspar glass dissolves considerable quartz.

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[1] Trans. Ceram. Soc. (Eng.), XXIII, p. 326, 1923–24.

[2] Jour. Soc. Glass. Tech., II, p. 177–216, 1918.

[3] Wilson, G. V., Jour. Soc. Glass. Tech., II, p. 177, 1918.

[4] Ann. soc. geol. Belg., XLVII, p. 174, 1919; Rev. Geol., 4, p. 297, 1923.

[5] Jour. Japan. Ceram. Assoc., 370, p. 238, 1923.

[6] U. S. Bur. Stand., Tech. Pap. 80.

Klein points out in another paper, however, that time and temperature are both factors influencing the constitution and microstructure of a porcelain body.[1] Thus a sample fired at cone 15 and soaked for one hour developed comparatively large crystals of "sillimanite" and extensive solution of the quartz, while one fired 1–6 times to cone 13–14, with a soaking period of twelve to eighteen hours, showed amorphous "sillimanite" and only slight solution of the quartz.

Peck,[2] on the other hand, says it does not seem possible to judge the burning temperature of porcelain bodies from a petrographic study without knowledge of the body composition and length of firing.

Commercial ware ranges from a low-burned porous whiteware, in which except for dehydration of the clay, only the feldspar is changed, to high-fired chemical porcelain, which consists of glass, sillimanite crystallites and residual quartz. He notes the absence of tridymite or cristobalite, from which he concludes that the quartz dissolves more readily in feldspar glass, than it inverts to other modifications.

Somers [3] made a petrographic examination of a series of high grade clay samples that had been fired for eight hours up to 950° C., and were then refired for eight hours to 1150° C., while another set was refired for ten hours up to 1300° C. In most of those fired to 1150° C. there was a development of isotropic material, which in most cases had increased in the 1300° C. burn. In the latter set one case of what was taken to be sillimanite (probably mullite) development was found. Corrosion of the quartz was noted in a few instances, and might have been more widespread had the heating been prolonged. Tourmaline and probably epidote seemed to disappear at 1150° C., but rutile, titanite and zircon were still recognizable at 1300° C. The hydromicas seemed to be isotropic at 1150° C.

Heat absorbed and evolved during firing and cooling.—Navias [4] determined the heat absorbed in raising clays to 1200° C., and that evolved during cooling. Four clays were studied: (*a*) A 1 English china-clay, (*b*) North Carolina kaolin, (*c*) Tennessee ball-clay No. 5, and (*d*) Laclede-Christy raw flint-clay. The results obtained were as follows: (1) All four clays contained about 14 per cent moisture in the air-dried condition, (2) up to 420° C., during which all the hygroscopic and some combined water are driven out, all four clays absorbed about the same amount of heat, 0.46 cal. per gram per 1°, (3) between 420° C. and 900° C. the remainder of the combined water is driven off. During this period clays (*b*) and (*d*) show the same heat absorption. About 0.7 cal. per gram per 1°. Clay (*a*) absorbed 0.95 and (*c*) only 0.53 cal. (4) During the final period, 900° C.–1200° C., clays (*b*) and (*d*) again show the same heat absorption, about 0.2 cal. per gram per 1°. Clay (*a*) showed only 0.075 cal. absorption, which is less than the specific heat, and hence indicates a heat-evolving action. (5) All four clays show the same total heat absorption (0.5 cal. per gram per 1°) over the whole firing period.

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[1] Jour. Amer. Ceram. Soc., III, p. 978, 1920.

[2] Jour. Amer. Ceram. Soc., II, p. 175, 1919. See also Mellor, Trans. Ceram. Soc. (Eng.), XVI, p. 71, 1917; Klein, Trans. Amer. Ceram. Soc., XVIII, p. 377, 1916; Mellor and Heath, Trans. Ceram. Soc. (Eng.), VII, p. 80, 1907.

[3] U. S. Geol. Surv., Bull. 708, p. 302, 1922.

[4] Jour. Amer. Ceram. Soc., VI, p. 1268, 1923.

FUSIBILITY

The fusing or softening point of a clay would theoretically be a point in the temperature scale at which the material passes from a solid to a fluid condition.

Since, however, the clay is a more or less heterogeneous mixture made up of mineral particles of different fusibilities some of which individually do not fail suddenly, it is difficult to speak of a definite fusing-point. Furthermore, as explained under vitrification, fusion proceeds progressively within the mass as the temperature is raised.

We can see, however, that as the temperature rises, there finally comes a point where so much of the material has softened as a result of fusion that the mass is no longer able to hold its shape.

In ceramic work the common method employed to determine the fusing or softening point [1] of a clay is to form the clay into a pyramidal piece, similar in shape and proportions to the standard pyrometric cones.

The softening point is considered to have been reached when the cone has bent over until the tip touches the base.

This condition may be reached without all the material of the clay having been actually fused or fluxed as for instance in the case of a clay containing coarse grains of sand surrounded by clay substance of much lower fusibility. When the clayey material becomes thoroughly softened by fusion the mass may bend over, even though the sand grains still retain their identity.

The temperature at which clays fuse naturally shows a wide range, the fusion-point being affected by (1) the amount of fluxing impurities present; (2) the texture, such as size of grain of refractory and non-refractory particles; (3) the homogeneity of the mass; (4) the conditions of the fire, whether oxidizing or reducing; and (5) the form of chemical combination of the elements in the clay.

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[1] The term squatting point and deformation point are also used.

Effect of chemical composition on fusibility.—As early as 1868, Richters[1] pointed out that if we start with pure kaolin, whose fusing-point is supposed to be cone 35, and add increasing amounts of silica the fusion-point of the mixture is lowered, until a mixture consisting of about 81 per cent SiO_2 and 19 per cent kaolin ($Al_2O_3 \cdot 17SiO_2$) is reached, whose fusion-point is about cone 26.

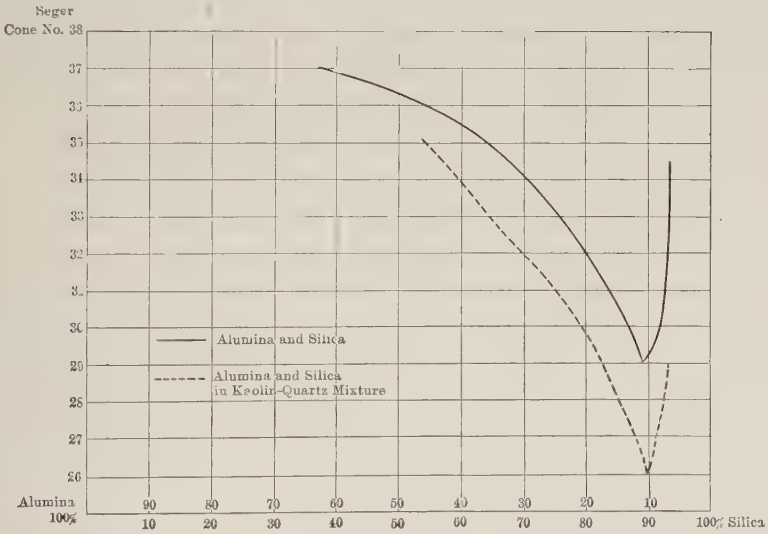

Fig. 93.—Diagram showing effect of silica on the fusion-point when mixed with alumina and with kaolin. (From Seger's experiments.)

Similar tests were tried by Bischof,[2] and later described by Seger,[3] who expressed the fusion-points graphically, using one curve to express the fusion-points of a mixture of alumina and silica, and a second curve for a mixture of Zettlitz kaolin and silica. Since the former contained a small amount of potash, a small quantity of feldspar was added to each of the mixtures to keep the alkali content constant (Fig. 93).

In both curves, which were originally graphed according to molecular weights, the eutectic was at the same $Al_2O_3 : SiO_2$ ratio, but was lower for the kaolin-quartz mixture than for the alumina-silica, which was cone 29.

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[1] Dingl. Polytech. Jour., CXCI, p. 59, 1869.

[2] Die feuerfeste Thone, 2nd ed., p. 61; also Dingl. Jour., CC, p. 289, 1871.

[3] Gesam. Schr., p. 435, 1896; Collected Writings, I, p. 545.

If now a pure clay in addition to containing silica, also contains so-called fluxing ingredients such as iron oxide, lime, magnesia and alkalies the fusion-point will be still further lowered.

It might be said in a general way that other things being equal, the temperature of fusion of a clay will fall with an increase in the percentage of total fluxes. If we compare the analyses of a brick-clay and a fire-clay, we shall find that the analysis of the former shows perhaps 12 to 15 per cent of fluxing or fusible ingredients, while that of the latter may show only 2 or 3 per cent, and that their fusion-points are perhaps 1093° C. and 1644° C., respectively. But while in general the fusion-point falls as the percentage of fluxes rises, it is thought that the different fluxes exert a different fluxing influence; that is to say, it requires more of one than another to bring about the same degree of fusibility. Moreover, there is a variation in the temperature at which the different ones become active.

One of the first investigators to throw some light on this subject was a German by the name of Richters. He formulated three laws, as follows:

1. The refractory quality of a clay of any given proportion of silica and alumina is most influenced by the fluxes in the following order: MgO, CaO, FeO, Na_2O, K_2O.

2. Chemically equivalent quantities of these oxides exert equal influences on the refractoriness of a given clay; that is, 40 parts of magnesia, 56 parts of lime, 72 parts of ferrous oxide, 62 of soda, and 92 parts of potash will each produce an equal degree of fusion in the same quantity of the same clay.

3. If a number of fluxes are present in a clay, the fusibility produced will be proportional to the sum of their chemical equivalents. For example, a clay with the formula

$$\left.\begin{matrix} 0.15\ K_2O \\ 0.15\ CaO \end{matrix}\right\},\ Al_2O_3,\ 2SiO_2$$

should fuse at the same temperature as one of the composition

$$\left.\begin{matrix} 0.1\ K_2O \\ 0.1\ CaO \\ 0.1\ FeO \end{matrix}\right\},\ Al_2O_3,\ 2SiO_2.$$

In working out these laws, Richters used a series of alumina-silica mixtures, to which known proportions of the fluxes were then added.

In his first series he employed silica and alumina mixed in the same proportions as in kaolinite, while in a second but similar series he used a higher silica percentage than is present in kaolinite.

Considering the case of silica and alumina in the proportions that they exist in kaolinite, it is found that they have a fusion-point of about 1830° C., or cone 36 of the Seger scale. The continued addition of silica to this lowers its fusion-point until the ratio of Al_2O_3, $17SiO_2$ (or 1 : 10 by weight), is reached, the fusion-point of this being about 1650° C., or cone 29, but a continued increase of silica raised it.

Silica, therefore, is to be regarded as a flux to alumina, at high temperature, and should not, therefore, be present in excess in refractory clays.

Moreover, the presence of silica in a clay seems to intensify the effect of other fluxes.

Cramer [1] at a later date attempted to verify Richter's experiments, but found that the fluxing power of oxides is only true in so far as it concerns kaolinite, while in the presence of free silica he found the fluxing power as follows: FeO, MgO, CaO, Na_2O, K_2O. In other words, if free silica is present the oxides do not act according to their chemical equivalency, 72 parts of ferrous oxide, for example, being more effective than 40 parts of magnesia, etc.

Rieke [2] in duplicating Richter's work in 1910, obtained somewhat different results.

He pointed out that the effect of equimolecular amounts of the different basic oxides is not the same in lowering the softening temp, and that even Cramer's curves showed this.

Thus in the alkaline earth group the oxides of the lowest molecular weight were found to lower the softening point most markedly, and those of higher molecular weight, least, considering equivalent additions.

Flack [3] obtained similar results.

Important as the results of Richter and Cramer are, the laws do not hold true for the changes ordinarily taking place in a kiln, even though they be burned to vitrification. That is to say, the law only holds true when all the elements of the clay can take part in the fusion of the mass; in other words, when it has reached a state of complete fusion.

In the melting of a clay, a reaction occurs between the silica, alumina, and the various fluxes, giving rise to the formation probably of complex silicates, and it is supposed that the various elements enter into combination in the same form. Thus iron, whatever its state of oxidation in the clay, is believed to enter into combination in the ferrous form, and therefore its fluxing power is regarded as due to the action of ferrous oxide. So, too, lime enters into combination as CaO, magnesium as MgO, and sodium and potassium as Na_2O and K_2O, respectively.

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[1] Tonindus.-Zeit., Nos. 40 and 41, 1895.

[2] Sprechsaal, XLIII, p. 198, 229, 314.

[3] Sprech., XLIV, pp. 171, 187, 205, 219.

Richter's work on the fusilibity of clays has been more recently discussed by Ludwig [1] from the view-point of modern chemical theories:

"The fusion of silicates results in the production of igneous solutions holding dissolved various silicates. Thus Seger cone No. 1 consisting of a mixture of feldspar, kaolin, quartz, and ferric oxide, is, when fused, a mutual solution of feldspar, quartz, augite or hornblende. If we could cool this mass slowly, these silicates would crystallize out one after the other. This has actually been done by Prof. Vogt of Christiania, who has shown that the temperature of fusion is always highest when only one definite silicate crystallizes out, and lowest when it represents a mixture of several silicates. This coincides perfectly with the general phenomenon observed in all solutions, namely, that, on dissolving any substance, a decrease of the melting-point takes place. It is immaterial whether the melting-point lies at 0° or at 1200° C. The compositions of the slags and glazes are practical illustrations, inasmuch as the most fusible combinations of either kind of silicate are always the most complex ones. When two silicates are combined, they invariably result in a mixture having a lower melting-point than either, owing to the formation of the so-called eutectic mixture. Thus, mono-calcium silicate fuses at cone 15; on adding one molecule of silica to two molecules of this silicate, the melting-point falls to cone 7, but on adding more quartz the fusion-point again rises. Again, in a clay containing besides silica and alumina the various fluxes, the melting-point is governed by the fusing-point of the eutectic mixture of these constituents, which represents the most fusible combination possible. This explains also why feldspar begins its fusing effect in a body much below its melting-point. The eutectic mixture is invariably high in fluxes at the lower temperatures, but takes up more and more silica as the temperature is raised. Silicates proper are more fusible than high alumina mixtures, and hence more silica is brought into solution than alumina, which is dissolved only at high temperatures. This explains the fact that aluminous clays show the greatest refractoriness. As the solution increases in amount the clay softens, and finally, when there remains but little undissolved matter, fusion takes place. This manner of melting is characteristic of solutions while substances homogeneously crystalline melt suddenly without softening. Thus the final melting-point depends upon the ratio of the alumina to the silica and the amount and kind of flux.

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[1] Tonindustrie-Zeitung, XXVIII, p. 773, 1904. The abstract of the paper here given is that of Bleininger, Trans. Amer. Ceram. Soc., VII, p. 275, 1905.

" The foundation of these fusion phenomena is the following general law applying to dilute solutions:

" Equi-molecular quantities of different substances dissolved in equal amounts of the same solvent lower the melting-point in the same degree.

" The law applies to substances in general, indifferent as to whether they are bases or acids, the only requirement being that they are soluble. With reference to clay we must therefore consider lime, magnesia, potash, soda, and titanic acid as the dissolved substances.

" If now we are to compare refractory clays as to their melting-points we must calculate the molecular formula of each clay, making the alumina equivalent equal to unity and adding the equivalents of various fluxes, obtaining thus a formula like

$$Al_2O_3 + 2.125SiO_2 + 0.0755RO.$$

" Since in this expression there are but two variables, Ludwig plotted the silica equivalent as the abscissa of a curve and ten times the equivalent of the RO as the ordinate, and in this manner he located various German fire-clays in a chart, verifying the clays by their melting-points in Seger cones.

" Richter's law, strictly speaking, applies only to dilute solutions, and hence if the amount of fluxes is considerable the law loses much of its force. It does not apply, therefore, completely to glazes or glasses. Differences from this general law are not due to chemical reasons, since it does not matter in what chemical combination a flux enters into a clay, whether as feldspar or as potash, but must be sought for in the different mechanical conditions.

" Ludwig summarizes his work in the following conclusions:

" 1st. Richter's law is a special case of the general law of dilute solutions.

" 2d. This law is restricted by the following conditions:

" (*a*) It applies only to very dilute solutions, that is clays with a small amount of fluxes and not to brick-clays or glazes.

" (*b*) It assumes intimate mixture.

" (*c*) Iron shows a different effect, due to its two stages of oxidation, since one molecule of ferric oxide corresponds to two molecules of ferrous oxide. A given percentage of iron contains fewer molecules of ferric oxide than of ferrous oxide, since the former has a higher molecular weight. On changing to the ferrous oxide the number of molecules is doubled, and hence the fluxing effect is doubled.

"3d. The analysis of a fire-clay is of great importance in estimating the refractoriness.

"4th. The estimation of the refractoriness by means of the percentages of alumina and fluxes leads to erroneous results."

A somewhat interesting chart has been prepared by Ludwig for determining the refractoriness of a clay from its chemical composition.

It is based on the assumption that the clays are solid solutions of the mineral impurities of the clay. If this view is true, they would reduce the melting-point in proportion to their molecular concentration.

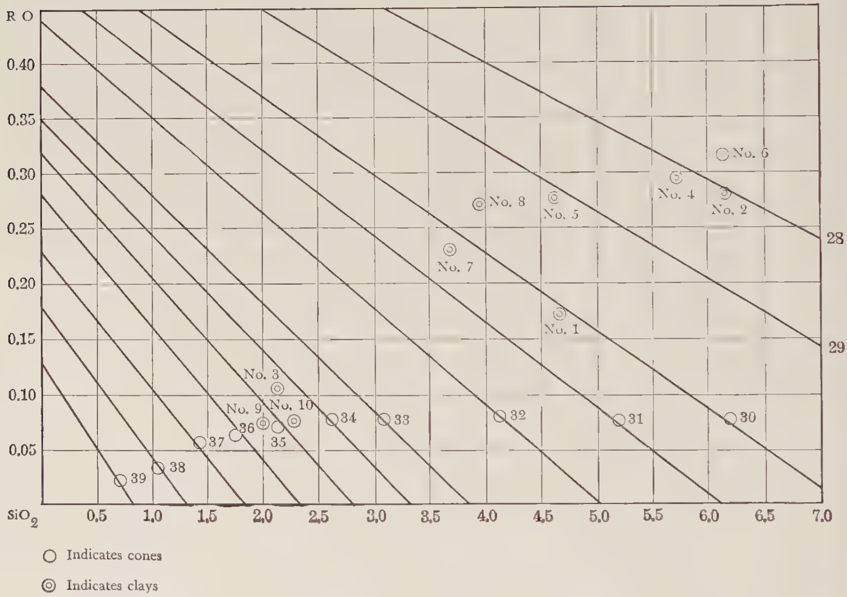

Fig. 94.—Ludwig's fusibility chart.

Ludwig determined the refractoriness of a number of clays, and then calculated their formula, as $xRO \cdot Al_2O_3 \cdot ySiO_2$, assuming alumina as unity. His calculations are given in the following table:

The refractoriness of the clays was plotted on a graph (Fig. 94), with the molecular ratios RO as ordinates, and SiO_2 as abscissae. Plotting the iso-refractory lines corresponding to the Seger cones on this graph, the refractoriness of a clay whose composition is included in the chart may be determined. The chart is said to be of little value for clays containing above 6 per cent RO bases.

To apply Ludwig's formula, one must have a chemical analysis of the clay, the making of which involves much more time than needed for

Number on chart	Analysis						Formula Al_2O_3 = unity						Sum of formula		Melting point	
	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O			Actual	Chart
1	70.70	25.80	2.36	.31	......	.89	4.656	1	.116	.022	......	.034	Al_2O_3, 4.65SiO_2	.176RO	29.30	30.31
2	73.84	20.54	4.43	.08	......	.14	6.112	1	.274	.007	......	.007	Al_2O_3, 6.11SiO_2	.288RO	19.20	28
3	53.99	43.21	2.43	.11	.28	.37	2.124	1	.072	.004	.0165	.009	Al_2O_3, 2.12SiO_2	.102RO	33.34	34.35
4	73.07	21.74	3.50	.41	.26	1.00	5.710	1	.205	.034	.003	.050	Al_2O_3, 5.71SiO_2	.293RO	31.32	28.29
5	68.60	26.10	3.75	.45	.29	.79	4.450	1	.047	.008	.007	.008	Al_2O_3, 4.51SiO_2	.273RO	32.33	29.30
6	74.43	20.61	3.15	.43	.18	1.20	6.130	1	.193	.039	.019	.064	Al_2O_3, 6.13SiO_2	.317RO	31.32	27.28
7	64.90	30.25	3.05	.47	.69	.49	3.65	1	2.30				Al_2O_3, 3.65SiO_2	.230RO	32	30.31
8	67.50	27.95	2.55	1.22	1.25	.25	3.95	1	2.70				Al_2O_3, 3.95SiO_2	.270RO	29	29.30
9	45.68	38.54	.90	.08	.38	.66	2.02	1	.030	.003	.025	.019	Al_2O_3, 2.01SiO_2	.077RO	35	35
					TiO_3						TiO_3					
10	47.69	38.15	.077	.21	.12	1.28	2.12	1	.026	.010	.004	.036	Al_2O_3, 2.12SiO_2	.077RO	35	35

RATIONAL ANALYSIS

	Clay number									
	1	2	3	4	5	6	7	8	9	10
Clay substance	62.42	53.83	94.03	51.31	62.07	48.27	....	....	96.55	
Feldspar	4.81	1.30	5.97	4.92	1.52	4.62	....	....	1.15	
Quartz	32.77	44.87	....	44.10	36.41	47.11	....	....	2.30	

an actual fusion test. It seems also to be applicable only to relatively pure clays. Attempts made to check it with a series of Iowa clays[1] show that out of sixty clays plotted, for which the fusion-points had already been determined, there was actual agreement in only six cases, and usually the actual fusion-points were five to six cones lower than those indicated by the chart.

A series of British fire-clays,[2] all above cone 28 in fusing-point, were plotted on the Ludwig chart, and the " agreement between the observed and the calculated results is fairly good, but discrepancies occur which may amount to as much as two cones."

Kaolin, Quartz, Feldspar Mixtures.—It was found by M. Simonis,[3] that of a series of mixtures of these three substances, the mixtures of feldspar and kaolin fused at higher temperatures than feldspar-quartz mixtures, although the melting-point of the quartz was higher than that of the kaolin. With a content of 70 per cent of feldspar the two curves were found to intersect. With 85 per cent feldspar the kaolin mixture fused lower than the corresponding quartz mixture. The fusion curve of kaolin and quartz showed the minimum fusing-point to be 1 molecule Al_2O_3 to 17 molecules of SiO_2. The minimum fusing-point of 25 per cent kaolin and 75 per cent quartz was found to lie between cone $26\frac{1}{2}$ and $26\frac{3}{4}$. The table on p. 301 shows the melting-points of a number of feldspar-quartz-kaolin mixtures:

Simonis plotted the compositions on a triaxial diagram and connected the points by isothermals. In this way the two refractory areas, one high in clay the other high in quartz, are clearly located as well as the areas of soft porcelain, whiteware, and hard porcelain. The feldspar invariably acts as a neutral and constant flux. Hence, in order to determine the melting-point of a porcelain or whiteware mixture, it is necessary only to divide the clay and quartz into the ratio of 1 : 3 and to consider the balance as raising and the feldspar content as lowering the fusibility. This consideration applied only to bodies containing not more than 60 per cent feldspar, and the mode of calculation is simply a practical one which has worked out very well in practice. If the percentages of kaolin, quartz, and feldspar are z, qu, and f, for bodies high in clay in which $z > \frac{qu}{3}$, the refractory index $= z - \frac{qu}{3} - f + 60$. For bodies high in quartz, where

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[1] Beecher, Ia. State College, Eng. Exper. Sta., Bull. 40, 1915.

[2] Enos and Scott, Mem. Geol. Surv. Gr. Brit., XXVIII, 1924.

[3] Sprechsaal, No. 29, p. 390, and No. p. 30, 402, 1907. Abstracted by Bleininger, Amer. Chem. Soc. Abstracts.

Zettlitz kaolin, per cent	Quartz, per cent	Feldspar, per cent	Melting-point in Seger cones	Zettlitz kaolin, per cent	Quartz, per cent	Feldspar, per cent	Melting-point in Seger cones
....	15	85	9–10	30	55	15	26
....	30	70	14	30	70	....	27
....	45	55	15–16	45	....	55	26
....	55	45	17	45	15	40	26–27
....	70	30	26–27	45	30	25	27–28
....	85	15	30–31	45	45	10	29
15	....	85	9	45	55	....	29–30
15	15	70	10–11	55	....	45	28
15	30	55	13–14	55	15	30	29–30
15	45	40	15	55	30	15	30+
15	55	30	17–18	55	45	....	30–31
15	70	15	–26	70	....	30	31+
15	85	....	28–29	70	15	15	32
30	....	70	14	70	30	....	32+
30	15	55	16–17	85	....	15	33–34
30	30	40	17–18	85	15	....	33–34
30	45	25	–26				

$\frac{qu}{3} > z$, the index $= \frac{qu}{3\ 2} - z - f + 60$. For the purpose of obtaining the value of the refractory index in terms of the Seger cones, the following table is given:

Refractory index.......	17.5	22.6	28	33.7	39.2	44.6	50	57.6
Seger cone.............	14	15	16	17	18	19	20	26
Refractory index.......	65	72	80	89	102	114	127	141
Seger cone.............	27	28	29	30	31	32	33	34

The melting-points of these mixtures were determined in electric carbon resistance furnaces.

Montgomery and Fulton have pointed out after studying the composition and softening point of fifty-seven refractory clays that (1) the $SiO_2 - Al_2O_3$ eutectic curve limits the refractoriness of a clay;[1] (2) the drop below this eutectic line in cones depends primarily upon the per cent of flux present; (3) as the amount of flux increases its activity increases rapidly; and (4) about 14 to 18 per cent alumina (based on alumina plus silica = 100) will give the maximum activity of the fluxes present.

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[1] Trans. Amer. Ceram. Soc., XIX, p. 303, 1917.

Bischof's formula.—One of the earliest developed was that of Bischof,[1] whose expression, termed the *Feuerfestigkeits-Quotient,* is as follows:

$$\text{F.Q.} = \frac{(\text{Oxygen in } Al_2O_3)^2}{(\text{Oxygen in RO})\ (\text{Oxygen in } SiO_2)},$$

in which RO represents the sum of the fluxes, each considered as the protoxide. The F.Q. may range from a small decimal to 25.

According to this formula the fusibility of a clay will vary directly as the square of the oxygen in the alumina, and inversely as the oxygen in the fluxes and silica, and Bischof concluded that the amount of alumina in a clay practically influenced its fusibility.

Bischof, on the basis of this formula, classified fire-clays into seven types or groups, in which the most refractory has a value for F.Q. of 14, and the least refractory that is used for fire-brick has a value of 1.6. He selected seven type clays, which he considered representative of each of these groups.

Objections to Bischof's formula have been stated by Wheeler [2] as follows:

"1. That while an increase in the percentage of alumina decreases the fusibility, when it becomes very high it acts the part of an acid instead of a base and tends to lower the fusing-point, or the reverse of Bischof's formula when this point is reached; neither does the fusibility decrease when the alumina is in moderate amounts, at the rapid rate of the square of the alumina.

"2. When the silica is present in amounts greater than a monosilicate (which is always the case with clays), the fusibility decreases as the silica increases, which is just the reverse of Bischof's formula.

"3. As a broad rule, the fusibility increases as the bases increase, at least to the extent that they occur in clays; but there is a very great range of fusibility according to the bases that are present. The alkalies are more readily fusible than the ferrous oxide, and this in turn than the lime or magnesia. Again a mixture of bases is more fusible than a single base, and the greater the number of bases the greater the fusibility. Bischof's formula, however, pays no attention to the bases present, or the number of them.

"4. Again equal weight is given to all fluxes, and all physical factors are ignored.

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[1] Die feuerfesten Thone, p. 116.

[2] Mo. Geol. Surv., Vol. XI, p. 146, 1896.

Seger's formula.—H. Seger,[1] recognizing the unsatisfactory character of Bischof's formula, suggested the following substitute:

$$F.Q. = \frac{(Al_2O_3)_2}{RO \times SiO_2} + \frac{Al_2O_3}{RO}.$$

While this formula gives better results, it likewise neglects porosity and texture.

Wheeler's formula.—Wheeler [2] has suggested a formula for expressing the relation between the detrimentals and non-detrimental constituents of a clay, which he terms the *Fusibility factor*. It is

$$F.F. = \frac{N}{D + D'},$$

in which N = sum of total silica, alumina, titanic acid, water, and carbonic acid;
D = total fluxes, namely, alkalies, iron oxide, lime, magnesia;
D′ = sum of alkalies.

This formula makes no distinction between free and combined silica and assumes that silica in a free state does not act as a flux. The alkalies are added twice, because of their supposed greater fluxing power. This formula is applicable however only to clays which are physically alike.

For those differing physical properties Wheeler suggests the fusibility factor

$$F.F. = \frac{N}{D + D' + C},$$

C having these values: C = 1 when clay is coarse grained and specific gravity exceeds 2.25;
C = 2 when clay is coarse grained and specific gravity ranges from 2 to 2.25;
C = 3 when clay is coarse grained and specific gravity ranges from 1.75 to 2.00;
C = 2 when clay is fine grained and specific gravity is over 2.25;
C = 3 when clay is fine grained and specific gravity is from 2 to 2.25;
C = 4 when clay is fine grained and specific gravity is from 1.75 to 2.25.

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[1] For discussions on development of this formula, see Collected Writings of Seger, Translation, I, p. 486, 1902.

[2] Mo. Geol. Surv., Vol. XI, p. 149, 1896.

While this formula is a step in the right direction, it is not altogether satisfactory, as, for example, the values are not specific because there is no accurate method of expressing the fineness. Moreover, the specific gravity is not the true specific gravity.

There is, after all, some question in the author's mind whether a formula involving the necessity of at least a chemical analysis and specific-gravity determination is any more valuable than a statement of the actual temperature or cone of fusion.

Effect of texture.—It seems hardly necessary to point out that texture as well as distribution of the constituents must exert an important effect on the fusion-point of a clay. If the grains of the clay are not all very fine and the constituents uniformly mixed one can hardly expect a clay to fuse at the point indicated by Ludwig's or any other formula.

This fact was pointed out by Ries [1] using artificial mixtures of varying texture. The same writer has also called attention to the fact that some New Jersey fire-brick [2] showed a fusion-point of cone 33, which was considerably higher than the fusion-point of the silica-alumina ratio in them. On grinding the brick sufficiently fine to pass through a 100-mesh sieve, remolding into cones and heating, it was found that the fusion-point dropped to cone 27.

W. Schuen [3] has also pointed out the lack of agreement between the fusing-point of a number of clays and their composition as compared with Seger cones, and considers it due to difference in grain size. The additional point is made that the method of combination is not without influence on the fusibility.

The results of some experiments made by H. O. Hofman and B. Stoughton,[4] would seem to be contrary to the views expressed above, since they claim that fine grinding of fire-clays does not affect their refractoriness. It was very evident, however, that the materials they worked on were quite homogeneous, and in such cases texture would exert little influence on the fusibility.

METHODS OF MEASURING FUSIBILITY

The methods used for measuring the fusibility of clays may be divided into two classes, namely, the direct and indirect.

Direct methods.—The temperature at which a clay fuses is determined either by means of test-pieces of known composition or by some form of apparatus or mechanical pyrometer, the principle of which depends on the expansion of gases or solids, thermoelectricity, spectrophotometry, etc.

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[1] Trans. Amer. Inst. Min. Engrs., XXXV, p. 205, 1904.

[2] N. J. Geol. Surv., Fin. Rept., VI, p. 330, 1904.

[3] Keram. Rundschau, XXIII, p. 565, 1925.

[4] Trans. Amer. Inst. Min. Engrs., XXVIII, p. 440, 1898.

While there are many different forms of these on the market a few only, especially those which have been most commonly used, need be described.

Seger cones.—These test-pieces consist of a series of mixtures of clays with fluxes, so graded that they represent a series of fusion-points each being but a few degrees higher than the one next to it.

Fusible cones were really invented by Lauth and Voght,[1] but they were not put to a practical use until described by Seger in 1886. The materials which he used in making them were such as would have a constant composition, and consisted of washed Zettlitz kaolin, Rörstrand feldspar, Norwegian quartz, Carrara marble, and pure ferric oxide. Cone 1 melts at the same temperature as an alloy composed of one part of platinum and nine parts of gold, or at 1150° C. Cone 20 melts at the highest temperature obtained in a porcelain furnace, or at 1530° C. The difference between any two successive numbers is 20° C., and the upper member of the series is cone 42. Cone 36 is composed of a very refractory clay slate, while cone 35 is composed of kaolin from Zettlitz, Bohemia. A lower series of numbers was produced by Cramer, of Berlin, who mixed boracic acid with the materials already mentioned.

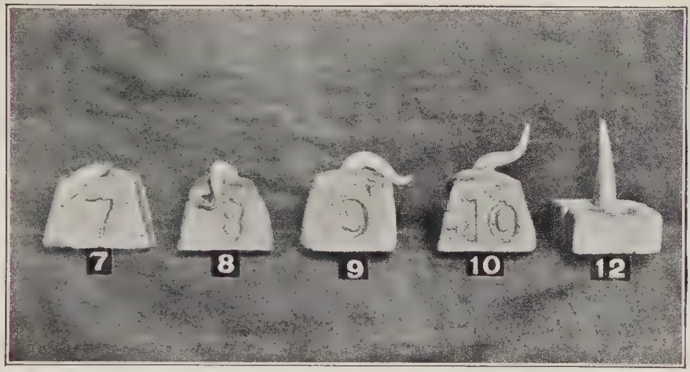

FIG. 95.—Seger cones used for determining heat effects in kilns. Nos. 7 and 8 were completely melted; No. 10 was slightly softened; No. 12 was unaffected; No. 9 was bent completely over, but not melted. The fusing-point of cone 9 was reached.

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[1] Bull. Soc. Chim., XLVI, p. 786, 1886.

Hecht obtained still more fusible mixtures by adding both boracic acid and lead in proper proportions to the cones. The result is that there is now a series of 64 numbers, the fusion-point of the lowest being 590° C. and that of the highest 2000° C. As the temperature rises the cone begins to soften, and when its fusion-point is reached it begins to bend over until its tip touches the base (Fig. 95). For practical purposes these cones are very successful, though their use has been somewhat unreasonably discouraged by some. They have been much used by foreign manufacturers of clay products and are widely used in the United States.

An important point to emphasize is that Seger cones are not intended to be used for measuring temperatures, even though their fusing-points are expressed in degrees temperature. Rather are they for the purpose of measuring pyrochemical effects.

Sosman [1] has pointed out that the existence and influence of eutectics seems to make temperature measurements by cones uncertain, and that to obtain sharp indications of temperature, unaffected by the rate of heating only pure compounds or pure eutectics can be used. A number of these occur among the silicates, which melt promptly at definite temperatures.

This limitation of cones as regards their use for temperature measurement has been noted by a number of other writers.[2]

Effect of time on melting-point.—Time appears undoubtedly to be an important factor in determining the deformation point of cones, and the fact has been brought out by several writers that slow heating in a large kiln, will cause a cone to bend over below its theoretic melting-point. Zimmer [3] has pointed out that with slow firing in a large biscuit kiln the cones 1 to 9 reached their melting-point, 25° C. to 30° C. lower than those placed in a small trial kiln whose temperature increased faster, but since it is heat effects and not degrees temperature that are being measured, this makes no difference.

Some definite figures on the effect of the rate of heating on the softening point of Seger cones, as determined by the Bureau of Standards [4] are given below:

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[1] Trans. Amer. Ceram. Soc., XV, p. 482, 1913.

[2] Bleininger and Brown, U. S. Bur. Stand., Tech. Pap. 7, 1912; Brown and Murray, Trans. Amer. Ceram. Soc., XV, p. 193, 1913; Fieldner, Hall and Field, U. S. Bur. Mines, Bull. 6, p. 129, 1918; Stover, Trans. Amer. Ceram. Soc., XV, p. 364, 1913; Lewis and Ries, Chem. Met. Eng., XXXIII, p. 153, 1926.

[3] Trans. Amer. Ceram. Soc., I, p. 23, 1899.

[4] U. S. Bur. Stand., Tech. Pap. 17, p. 27.

Softening Point of Seger (Orton) Cones, Heated at Different Rates

Cone	Rate of heating, ° C. per hour				Cone	Rate of heating, ° C. per hour			
	42.5	26.5	20.0	12.5		42.5	27.5	20.0	12.5
010	885	885	880	910	1	1100	1085	1090	1070
09	920	930	950	890*	2	1110	1090	1100	1075
08	950	970	970	965	3	1120	1110	1110	1080
07	960	975	950	970	4	1130	1125	1115	1090
06	990	1000	990	995	5	1140	1135	1125	1110
05	1015	1035	1025	1030	6	1170	1140	1135	
04	1040	1055	1040	1045	7	1185	1155	1140	1125
03	1055	1065	1050	1050	8	1200	1170	1160	1150
02	1065	1070	1065	1060	9	1230	1190	1180	1190
01	1080	1080	1080	1070					

* This figure may seem out of line, but G. H. Brown states that it is correct (private communication.)

Effect of kiln gases.—The action of kiln gases on iron-bearing cones especially has also been observed.[1]

Seger cones exposed to the action of a reducing atmosphere (coal gas) while heated in an electric furnace, were found to stand up at temperatures far above those at which they were supposed to melt, due to the formation of a superficial crust covered and impregnated with lustrous carbon. The interior of the cone was slagged.[2]

Appreciable amounts of sulphur or SO_2 may materially affect the end-points. Carbon may form a refractory skin on the surface of the cone and prevent it from bending even though the interior melts.[3]

Factors controlling behavior of cones.—The factors controlling the action of cones during their heat treatment are of two kinds.[4]

(*a*) Those controllable to a large extent by the maker, including: (1) Size and shape; (2) texture; (3) intimacy of mixture; (4) porosity and homogeneity; (5) chemical and mineralogical composition; (6) physico-chemical composition of materials and particles, including whether they are crystalline, colloidal, amorphous or glassy, and whether water of crystallization, dissolved or adsorbed gases, etc., are present, and (7) unknown factors controlled by fixed methods of making.

(*b*) Those controlled to a greater or less degree by uses: (1) Mount-ing and position; (2) oxidation of organic binder; (3) release of H_2O and CO_2; (4) rate of firing; (5) furnace atmosphere; (6) absorbed or deposited carbon in ceramic products.

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[1] Trans. Amer. Ceram. Soc., II, p. 60, 1900.

[2] Trans. Ceram. Soc. (Eng.), XXI, 1921–22; Gas World, LXXIV, p. 503, 1921.

[3] Henderson, H. B. Jour. Amer. Ceram. Soc., IX, p. 740, 1926.

[4] Fairchild and Peters, Jour. Amer. Ceram. Soc., IX, p. 106, 1925.

From time to time various observers have redetermined the fusion points of different parts of the series and have usually come to the conclusion that the fusion temperatures needed revision.[1]

The most recent determinations of the melting-points of cones are those made by Fairchild and Peters.[2] They determined the temperatures of the end-point of a complete set of cones at carefully controlled rates of heating in clean air and in various kiln gases. They state that with " few exceptions the end-points were found to be higher when the rate of heating was 150° C. per hour than when the rate was 20° C. per hour. Under slow heating in gases free from SO_2 the end-points of cones .015 to .01 are somewhat higher than those shown in clean air. Cones .022 to .016 and 1 to 42 were acted on only slightly by kiln gases free from SO_2."

Comparison of different makes of cones.—While the different members of any one make of cones are usually consistent with each other, the same numbers of different makes do not always agree. This fact was well brought out by H. E. Ashley,[3] who tested the different makes together, plotting the results of his tests in the table shown in Fig. 96. In this the Columbus cones are spaced equidistant for convenience. The temperature at which the cones are supposed to melt, as given by the Tonindustrie-Zeitung, are placed to the left of the Orton (Columbus) cones in the figure, while the temperature at which Geijsbeek[4] found them to melt are given in a corresponding column on the right of them. The column on the extreme right gives the melting-points of Holdcroft & Co.'s patent thermoscopes. These are straight, dry-pressed bars, placed horizontally with a support at either end. Under the influence of heat they sag in the middle.

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[1] Bleininger and Brown, U. S. Bur. Stand., Tech. Pap. 7, p. 15; Bradshaw and Emery, Trans. Ceram. Soc. (Eng.), XXI, p. 117, 1921–22; Cole, Jour. Amer. Ceram. Soc., VIII, p. 462, 1924; Geijsbeek, Trans. Amer. Ceram. Soc., VI, p. 94, 1904; and XIV, p. 849, 1912; Hofman, Tonind.-Zeit., XXI, p. 1366, 1907; Hottinger, Trans. Amer. Ceram. Soc., III, p. 183, 1902; Klug, Sprechs., LIX, p. 21, 1926; Loeser, ibid., XL, p. 499, 1907; Mellor, Trans. Ceram. Soc. (Eng.), VII, p. 79, 1910; Rieke, Keram. Rundsch., XLIV, p. 549, 1911; and XLIV, pp. 143 and 726, 1911; Rothe, ibid., XLIV, p. 481, 1907; Rothe, Tonind.-Zeit., XXXI, p. 1366, 1917; Simonis, Sprechs., XLI, p. 561, 1908, and p. 71, 1902; Sosman, Trans. Amer. Ceram. Soc., XV, p. 482, 1913; Zimmer, ibid., I, p. 23, 1899.

[2] Fairchild, C. O., and Peters, M. F., Jour. Amer. Ceram. Soc. IX, P. 701, 1926.

[3] Trans. Amer. Ceram. Soc., VIII, p. 159, 1906.

[4] Trans. Amer. Ceram. Soc., Vol. VI, p. 94, 1904. See also Cole, S. S., Jour. Amer. Ceram. Soc., VIII, p. 462, 1924.

End-points of Pyrometric Cones as Determined by Fairchild and Peters

Number of cone	Composition	End-point	
		Rate, 20° C. per hour	Rate, 150° C. per hour
022	$\left\{\begin{array}{l}0.5\ Na_2O\\ 0.5\ PbO\end{array}\right\}$ .... $\left\{\begin{array}{l}2.0\ SiO_2\\ 1.0\ B_2O_3\end{array}\right\}$	585° C.	605° C.
021	$\left\{\begin{array}{l}0.5\ Na_2O\\ 0.5\ PbO\end{array}\right\}$ $0.1\ Al_2O_3$ $\left\{\begin{array}{l}2.2\ SiO_2\\ 1.0\ B_2O_3\end{array}\right\}$	595° C.	615° C.
020	$\left\{\begin{array}{l}0.5\ Na_2O\\ 0.5\ PbO\end{array}\right\}$ $0.2\ Al_2O_3$ $\left\{\begin{array}{l}2.4\ SiO_2\\ 1.0\ B_2O_3\end{array}\right\}$	625° C.	650° C.
019	$\left\{\begin{array}{l}0.5\ Na_2O\\ 0.5\ PbO\end{array}\right\}$ $0.3\ Al_2O_3$ $\left\{\begin{array}{l}2.6\ SiO_2\\ 1.0\ B_2O_3\end{array}\right\}$	630° C.	660° C.
018	$\left\{\begin{array}{l}0.5\ Na_2O\\ 0.5\ PbO\end{array}\right\}$ $0.4\ Al_2O_3$ $\left\{\begin{array}{l}2.8\ SiO_2\\ 1.0\ B_2O_3\end{array}\right\}$	670° C.	720° C.
017	$\left\{\begin{array}{l}0.5\ Na_2O\\ 0.5\ PbO\end{array}\right\}$ $0.5\ Al_2O_3$ $\left\{\begin{array}{l}3.0\ SiO_2\\ 1.0\ B_2O_3\end{array}\right\}$	720° C.	770° C.
016	$\left\{\begin{array}{l}0.5\ Na_2O\\ 0.5\ PbO\end{array}\right\}$ $0.55\ Al_2O_3$ $\left\{\begin{array}{l}3.1\ SiO_2\\ 1.0\ B_2O_3\end{array}\right\}$	735° C.	795° C.
015	$\left\{\begin{array}{l}0.5\ Na_2O\\ 0.5\ PbO\end{array}\right\}$ $0.6\ Al_2O_3$ $\left\{\begin{array}{l}3.2\ SiO_2\\ 1.0\ B_2O_3\end{array}\right\}$	770° C.	805° C.
014	$\left\{\begin{array}{l}0.5\ Na_2O\\ 0.5\ PbO\end{array}\right\}$ $0.65\ Al_2O_3$ $\left\{\begin{array}{l}3.3\ SiO_2\\ 1.0\ B_2O_3\end{array}\right\}$	795° C.	830° C.
013	$\left\{\begin{array}{l}0.5\ Na_2O\\ 0.5\ PbO\end{array}\right\}$ $0.7\ Al_2O_3$ $\left\{\begin{array}{l}3.4\ SiO_2\\ 1.0\ B_2O_3\end{array}\right\}$	825° C.	860° C.
012	$\left\{\begin{array}{l}0.5\ Na_2O\\ 0.5\ PbO\end{array}\right\}$ $0.75\ Al_2O_3$ $\left\{\begin{array}{l}3.5\ SiO_2\\ 1.0\ B_2O_3\end{array}\right\}$	840° C.	875° C.
011	$\left\{\begin{array}{l}0.5\ Na_2O\\ 0.5\ PbO\end{array}\right\}$ $0.8\ Al_2O_3$ $\left\{\begin{array}{l}3.6\ SiO_2\\ 1.0\ B_2O_3\end{array}\right\}$	875° C.	905° C.
010	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $\begin{array}{l}0.2\ Fe_2O_3\\ 0.3\ Al_2O_3\end{array}$ $\left\{\begin{array}{l}3.50\ SiO_2\\ 0.50\ B_2O_3\end{array}\right\}$	890° C.	895° C.
09	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $\begin{array}{l}0.2\ Fe_2O_3\\ 0.3\ Al_2O_3\end{array}$ $\left\{\begin{array}{l}3.55\ SiO_2\\ 0.45\ B_2O_3\end{array}\right\}$	930° C.	930° C.
08	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $\begin{array}{l}0.2\ Fe_2O_3\\ 0.3\ Al_2O_3\end{array}$ $\left\{\begin{array}{l}3.60\ SiO_2\\ 0.40\ B_2O_3\end{array}\right\}$	945° C.	950° C.
07	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $\begin{array}{l}0.2\ Fe_2O_3\\ 0.3\ Al_2O_3\end{array}$ $\left\{\begin{array}{l}3.65\ SiO_2\\ 0.35\ B_2O_3\end{array}\right\}$	975° C.	990° C.
06	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $\begin{array}{l}0.2\ Fe_2O_3\\ 0.3\ Al_2O_3\end{array}$ $\left\{\begin{array}{l}3.70\ SiO_2\\ 0.30\ B_2O_3\end{array}\right\}$	1005° C.	1015° C.
05	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $\begin{array}{l}0.2\ Fe_2O_3\\ 0.3\ Al_2O_3\end{array}$ $\left\{\begin{array}{l}3.75\ SiO_2\\ 0.25\ B_2O_3\end{array}\right\}$	1030° C.	1040° C.
04	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $\begin{array}{l}0.2\ Fe_2O_3\\ 0.3\ Al_2O_3\end{array}$ $\left\{\begin{array}{l}3.80\ SiO_2\\ 0.20\ B_2O_3\end{array}\right\}$	1050° C.	1060° C.
03	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $\begin{array}{l}0.2\ Fe_2O_3\\ 0.3\ Al_2O_3\end{array}$ $\left\{\begin{array}{l}3.85\ SiO_2\\ 0.15\ B_2O_3\end{array}\right\}$	1080° C.	1115° C.
02	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $\begin{array}{l}0.2\ Fe_2O_3\\ 0.3\ Al_2O_3\end{array}$ $\left\{\begin{array}{l}3.90\ SiO_2\\ 0.10\ B_2O_3\end{array}\right\}$	1095° C.	1125° C.
01	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $\begin{array}{l}0.2\ Fe_2O_3\\ 0.3\ Al_2O_3\end{array}$ $\left\{\begin{array}{l}3.95\ SiO_2\\ 0.05\ B_2O_3\end{array}\right\}$	1110° C.	1145° C.
1	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $\left.\begin{array}{l}0.2\ Fe_2O_3\\ 0.3\ Al_2O_3\end{array}\right\}$ $4\ SiO_2$...........	1125° C.	1160° C.
2	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $\left.\begin{array}{l}0.1\ Fe_2O_3\\ 0.4\ Al_2O_3\end{array}\right\}$ $4\ SiO_2$...........	1135° C.	1165° C.
3	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $\left.\begin{array}{l}0.05\ Fe_2O_3\\ 0.45\ Al_2O_3\end{array}\right\}$ $4\ SiO_2$...........	1145° C.	1170° C.
4	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $0.5\ Al_2O_34SiO_2$.............	1165° C.	1190° C.
5	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $0.5\ Al_2O_35SiO_2$.............	1180° C.	1205° C.
6	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $0.6\ Al_2O_36SiO_2$.............	1190° C.	1230° C.
7	$\left\{\begin{array}{l}0.3\ K_2O\\ 0.7\ CaO\end{array}\right\}$ $0.7\ Al_2O_37SiO_2$.............	1210° C.	1250° C.

End-points of Pyrometric Cones as Determined by Fairchild and Peters—*Cont.*

Number of cone	Composition	End-point	
		Rate, 20° C. per hour	Rate, 150° C. per hour
8	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}0.8\ Al_2O_38SiO_2$	1225° C.	1260° C.
9	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}0.9\ Al_2O_39SiO_2$	1250° C.	1285° C.
10	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}1.0\ Al_2O_310SiO_2$	1260° C.	1305° C.
11	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}1.2\ Al_2O_312SiO_2$	1285° C.	1325° C.
12	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}1.4\ Al_2O_314SiO_2$	1310° C.	1335° C.
13	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}1.6\ Al_2O_316SiO_2$	1350° C.	1350° C.
14	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}1.8\ Al_2O_318SiO_2$	1390° C.	1400° C.
15	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}2.1\ Al_2O_321SiO_2$	1410° C.	1435° C.
16	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}2.4\ Al_2O_324SiO_2$	1450° C.	1465° C.
17	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}2.7\ Al_2O_327SiO_2$	1465° C.	1475° C.
18	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}3.1\ Al_2O_331SiO_2$	1485 °C.	1490° C.
19	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}3.5\ Al_2O_335SiO_2$	1515° C.	1520° C.
20	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}3.9\ Al_2O_339SiO_2$	1520° C.	1530° C.
21	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}4.4\ Al_2O_344SiO_2$		
22	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}4.9\ Al_2O_349SiO_2$		
23	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}5.4\ Al_2O_354SiO_2$	....	1580° C.
24	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}6.0\ Al_2O_360SiO_2$		
25	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}6.6\ Al_2O_366SiO_2$		
26	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}7.2\ Al_2O_372SiO_2$	In Arsem furnace at 600° C. per hour	1595° C.
27	$\left\{\begin{matrix}0.3\ K_2O\\0.7\ CaO\end{matrix}\right\}20\ Al_2O_3200SiO_2$		1605° C.
28	$Al_2O_3\ 10\ SiO_2$		1615° C.
29	$Al_2O_3\ 8\ SiO_2$	....	1640° C.
30	$Al_2O_3\ 6\ SiO_2$	....	1650° C.
31	$Al_2O_3\ 5\ SiO_2$	....	1680° C.
32	$Al_2O_3\ 4\ SiO_2$	....	1700° C.
33	$Al_2O_3\ 3\ SiO_2$	....	1745° C.
34	$Al_2O_3\ 2.5\ SiO_2$	1755° C.	1760° C.
35	$Al_2O_3\ 2\ SiO_2$	1775° C.	1785° C.
36	$Al_2O_3\ 1.5\ SiO_2$	1810° C.	1810° C.
37	$Al_2O_3\ 1.66\ SiO_2$	1830° C.	1820° C.
38	$Al_2O_3\ 1.33\ SiO_2$	1850° C.	1835° C.
39	$Al_2O_3\ 1.00\ SiO_2$	1865° C.	
40	$Al_2O_3\ 66SiO_2$	1885° C.	
41	$Al_2O_3\ 33\ SiO_2$	1970° C.	
42	Al_2O_3	2015° C.	

Similar differences between different makes of cones still exist.[1]

Use of cones.—In actual use the cones are placed in the kiln at a point where they can be watched through a peep-hole (Fig. 97), but at the same time will not receive the direct touch of the flame from the fuel. It is always well to put two or more cones of different numbers in the kiln, so that warning can be had, not only of the end-point of firing but also of the rapidity with which the temperature is rising.

In determining the proper cone to use in burning any kind of ware, several cones are put in the kiln, as, for example, numbers 08, 1 and 5. If .08 and 1 are bent over in burning and 5 is not affected the temperature of the kiln is between 1 and 5. The next time numbers 2, 3, and 4 are put in, and 2 and 3 may be fused, but 4 remains unaffected, indicating that the temperature reached the fusing-point of 3.

While the temperature of fusion of each cone is given in the preceding table, it must not be understood that these cones are for measuring temperature, but rather for measuring pyrochemical effects. Thus if certain changes are produced in a clay at the fusing-point of cone 5, the same changes can be reproduced at the fusion-point of this cone, although the actual temperature of fusion may vary somewhat, due to variation in the condition of the kiln atmosphere.

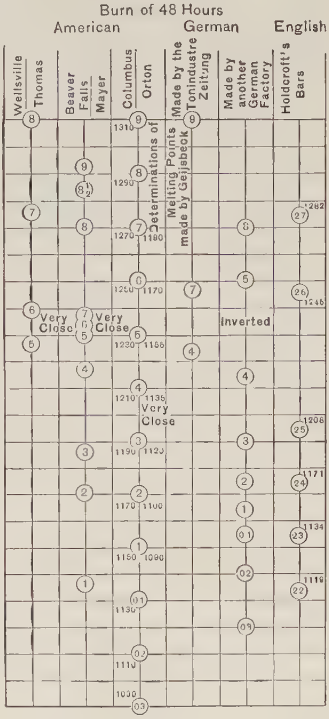

FIG. 96.—Diagram showing relative fusibility of different makes of cones. (Trans. Amer. Ceram. Soc., VIII, 1906.)

Manufacturers occasionally claim that the cones are unreliable and not satisfactory, forgetting that their misuse may often be the true reason for irregularities in their behavior. It is unnecessary, perhaps, to state that certain reasonable precautions should be taken in using these test-pieces. The cones are commonly fastened to a brick with a piece of wet clay, and should be set in a vertical position. After being placed in a position where they can be easily seen through a peep-hole, the latter should not be opened widely during the burning, lest a cold draft strike the cones, and a skin form on its surface and interfere with its bending. If the heat is raised too rapidly, the cones which contain much iron swell and blister and do not bend over, so that the best results are obtained by the slow softening of the cone under a gradually rising temperature. Aside from this, however, trouble has been experienced with cones numbers 010 to 3, which may act irregularly if exposed for any length of time to sulphurous fumes from the fuel, as in burning in some muffle-kilns, where there is not a free circulation of air in the muffle. The sulphuric acid appears to cause a volatilization of the boracic acid, and unites with the lime in the exterior of the cone, forming a hard skin of less fusible character than the interior, which melts while the outside is still hard. It has been suggested that the composition of these members of the cone series be changed. One set of cones cannot be used to regulate an entire kiln, but several sets should be placed in different portions of the same. One advantage possessed by cones over trial-pieces is that the cones can be watched through a small peep-hole, while a larger opening must be made to draw out the trial-pieces.

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[1] See detailed discussion by R. F. Geller and E. E. Pressler, Jour. Amer. Ceram. Soc., IX, p. 741, 1926.

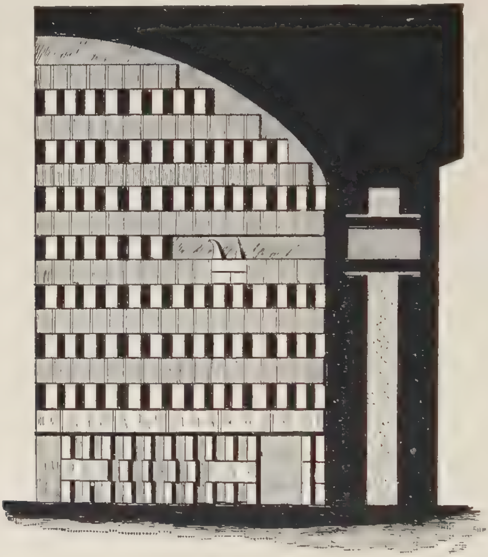

Fig. 97.—Section of kiln showing method of placing Seger cones.

Cones of fusion of different clays.—The following table gives the fusion-point in cones of a number of types of clay, the figures being compiled from different sources.

Fusion Point of Different Types of Clay in Cones

Type	Fusion point in cones
Washed kaolins	33 –35
White sedimentary kaolins, Georgia-South Carolina	34 –35
Ball clays	30 –35
Crucible clays	30 –33
Refractory bond clays	28 –33
Glass pot clays	21½–32
Flint clays, Maryland, No. 1 grade	32 –35
Plastic fire clays, No. grade	27 –35
Plastic fire clays, Maryland, No. 2 grade	31 –32
Flint clays, Maryland, No. 2 grade	28 –31
Ohio flint clays	31 –32½
Sagger clays	14 –31
Stoneware clays	18 –32
Face brick clays	17 –30.5
Common brick clays	1 –10

The cone numbers used in the different branches of the clay-working industry in the United States are approximately as follows:

Common brick		012–3
Hard-burned, common brick		1–2
Buff front brick		2–9
Hollow blocks and fireproofing		03–1
Terra cotta		02–7
Conduits		7–8
Fire-bricks		5–14
Red earthenware		010–05
Stoneware		6–8
Porcelain insulators		9½–11
White earthenware	Biscuit	8–9
	Glaze	6–7
	Some glaze at cone	3
China	Biscuit	11
	Glaze	7

Thermoelectric pyrometer.—This pyrometer is based on the principle of generating an electric current by the heating of a thermoelectric couple consisting of two wires of dissimilar metals. These two are fastened together at one end, while the two free ends are carried to a galvanometer which measures the intensity of the current. The metals used for the thermocouple will vary with the nature of the work and temperature to be measured. Thus copper-constantan (an alloy of copper and nickel) can be used for accurate work up to 360° C., and up to 500° C. with 5° to 10° C. error. For a temperature range of between 350° C. and 1100° C. alloys of chromium and nickel or of aluminum and nickel may be employed. For temperatures from 300° C. to 1500° C. a couple consisting of platinum, and an alloy of 90 per cent platinum and 10 per cent rhodium is used. The wires are enclosed in an outer and inner tube to keep them separated, and the outer tube closed at one end. These tubes may be of unglazed porcelain or fused quartz.

For much work, especially in clay-working plants, a recording instrument is highly desirable.

These pyrometers are widely used in laboratory and plant work. In the latter they serve to keep track of the rate of temperature rise and set backs.

Optical pyrometer.—This type of instrument measures the intensity of one definite wave length of the radiant energy emitted by a heated object, and by this means determines the temperature. The wave length measured is commonly that of red light, all others being filtered out by a red glass in the eyepiece.

One type consists of a telescope in the focus of which there is placed a small electric lamp, the filament of which is heated by a current from a battery, which is controlled by a rheostat and measured by an ammeter. The telescope is sighted on the object whose temperature is to be measured, and the current is adjusted until the filament is of the same brightness as the object. The temperature is then read from a table giving relation of filament current to temperature. This pyrometer can be used at higher temperatures than the platinum thermocouple. It has not been made automatically recording.

Wedgwood pyrometer.—This pyrometer, which has been used from time to time in ceramic establishments, depends on the shrinkage of clay cylinders, whose contraction is supposed to be proportionate to the temperature to which they are exposed. Their behavior is unreliable.

Indirect methods.—There are several indirect methods of determining fusibility, but that of Bischof[1] is perhaps the best known. This consists in increasing the refractoriness of weighed samples by adding to them increasing quantities of an intimate mixture of equal parts of chemically pure silica and alumina, and heating them with a prism of Saarau fire-clay (whose fusing-point is Seger cone 36) to above the melting-point of wrought iron. The amount of the mixture required to tone the clay up to the same refractoriness as the standard indicates its quality. It was used by Bischof chiefly for refractory clays.

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[1] Dingler's Polyt. Jour., Vol. CXCVI, pp. 438, 525, and CXCVIII, p. 396.

Hofman and Demond[1] tried the method of mixing various samples of fire-clays with varying proportions of calcium carbonate, and calcium carbonate and silica, to render them fusible at temperatures below the melting-point of platinum, while common brick-clays were mixed with alumina and silica to decrease their fusibility, the object being to arrive at a standard temperature at which both refractory and fusible clays could be tested. The results obtained at first were very satisfactory, but subsequent ones did not result as was desired and the method had to be abandoned.

More recently, however, this method has been tried by J. L. Newell and G. A. Rockwell with much better results.[3] In these last experiments the Seger cone 26 was used as a standard, as it was regarded as forming the line between refractory and non-refractory clays, the non-refractory ones being toned up until they showed the same behavior in the fire as cone 26. The amount of toner added then gave an idea how far the clay stood below the lower limit of refractoriness.

Analyses of Clays and Results of Tests

Sample number	26,* per cent	25,* per cent	3,* per cent	22,* per cent	24,* per cent	23,* per cent	1982,† per cent
SiO_2	64.10	55.60	57.10	57.45	57.15	49.30	43.94
Al_2O_3	21.79	24.34	21.29	21.06	20.26	24.00	11.17
H_2O comb.	6.05	6.75	6.00	5.90	5.50	9.40	3.90
Total	91.94	86.69	84.39	84.41	82.91	82.70	59.01
Fe_2O_3	2.51	6.11	7.31	7.54	7.54	8.40	3.81
CaO	0.10	0.43	0.29	0.29	0.90	0.56	11.64
MgO	0.58	0.77	1.53	1.22	1.62	1.60	4.17
K_2O	2.62	3.00	3.44	3.27	3.05	3.91	2.90
Na_2O	0.03	0.09	0.61	0.39	0.58	0.17	0.71
Total	5.84	10.40	13.18	12.71	13.69	14.64	23.23
Moisture	1.10	2.65	1.30	1.90	2.70	1.20	15.66‡
Grand total	98.88	99.74	98.87	99.02	99.30	98.54	98.00§
Stiffening ingredient, per cent	20	40	60	80	80	100	180

* N. W. Lord, anal. † E. Orton, Jr., anal. ‡ Includes CO_2. § Includes P_2O_5 0.10 per cent.

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[1] Trans. Amer. Inst. Min. Engrs., XXV, p. 3, 1896.

[2] Ibid., XXVIII, p. 435, 1899.

The silica used in the experiments was quartz, ground to pass a 100-mesh sieve and purified by boiling in nitrohydrochloric acid. It had 99.88 per cent silica. The alumina contained 98.48 Al_2O_3.

The method followed was to weigh out samples of 1 gram of the clay to be tested and mix them severally with 0.1, 0.2, 0.3, etc., grams of the silica-alumina mixture. The samples were then tested in the Deville furnace.

The table on p. 315 gives the results of the experiments just described, the clays being arranged in the order of their refractoriness, and in each case the amount of flux being given that was required to raise the fusing-point to that of cone 26 of Seger.

CHAPTER VI

KINDS OF CLAYS

In this chapter it is proposed to give briefly the characters of the clays employed for different purposes, beginning with the highest grades.

Kaolins

The term kaolin was originally used to refer to white residual clays of a white or nearly white burning character, but in recent years it has been stretched to cover certain white sedimentary clays like those obtained in South Carolina and Georgia. The author has always registered his opposition to such a grading which was done originally for commercial purposes. In order to avoid any confusion, the terms residual and sedimentary kaolins will be used here.[1]

Most residual kaolins as mined are rather siliceous, but in their washed condition approach closely to the composition of kaolinite, from which it has been sometimes been incorrectly argued that kaolins are composed chiefly of kaolinite and quartz.

Sedimentary kaolins may also require washing before shipment.

Kaolins are of particular value because of the need of their being used in both porous and vitrified whiteware. Much is still being imported from England for use in the United States and Canada, but American ones are now being employed in considerable quantity.[2]

Residual kaolins.—These as already explained are commonly formed by weathering processes, and from a number of different kinds of rock, but all of the different genetic types may be of commercial value.

Most kaolins as mined are rather siliceous, and consequently have to be put through a washing process to eliminate the sand before shipment to the market, and the refined product sometimes approaches kaolinite in its composition. If the sand in the kaolin is coarse to medium its separation causes relatively little trouble, but if very fine grained it may be difficult to eliminate thoroughly.

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[1] The washed kaolins of Cornwall has been referred to as *China Clay*, and the term is also used in this country. See further discussion in Trans. Amer. Ceram. Soc., XIV, P. 815, 1912, and Trans. Ceram. Soc. (Eng.), VIII, P. 27.

[1] For comparison of English and American clays see: Watts, A. S., Jour. Amer. Ceram. Soc., II, p. 151, 1919, and Fritz, E. H., ibid., VIII, p. 253, 1925.

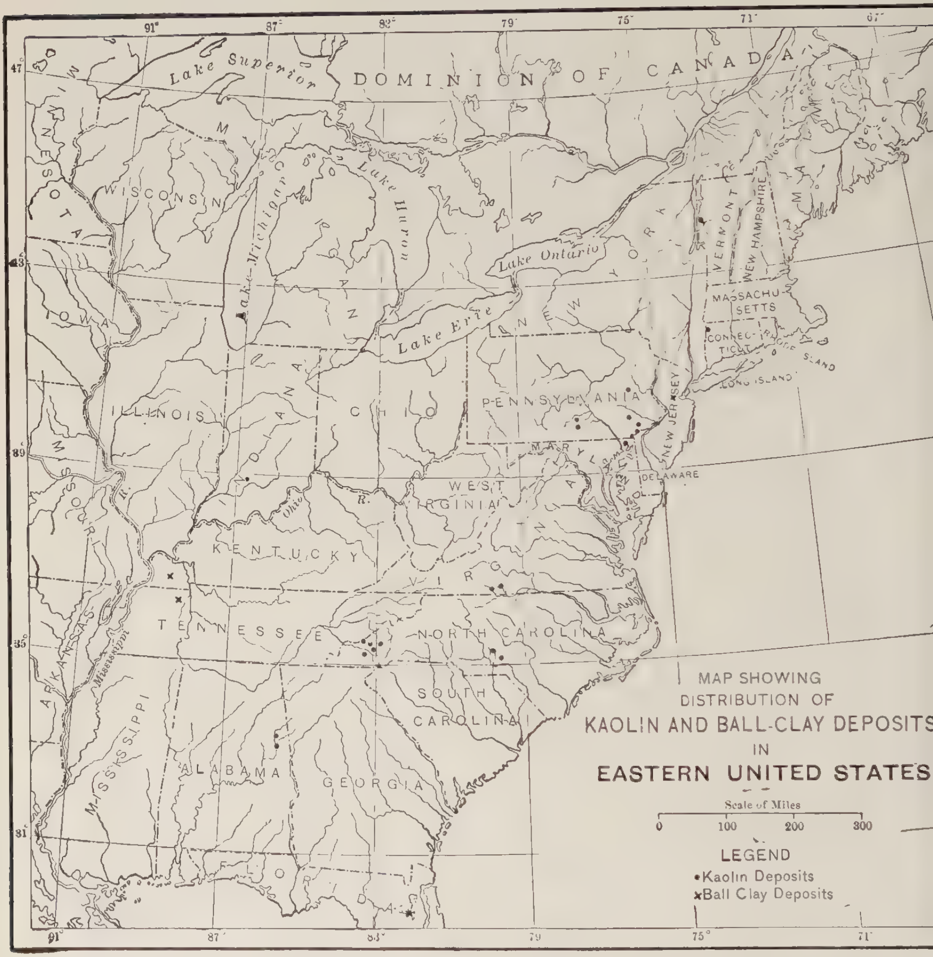

FIG. 98.—Map showing kaolin and ball-clay deposits of the United States, east of the Mississippi. (After Ries, U. S. Geol. Surv. Prof. Pap. 11, 1903.)

The washing is done by disintegrating the clay with water in blungers or log washers, after which the mixture floats along a great length of troughing where the sand settles out. The water and clay then passes into large tanks, where the clay settles to the bottom. From here it is

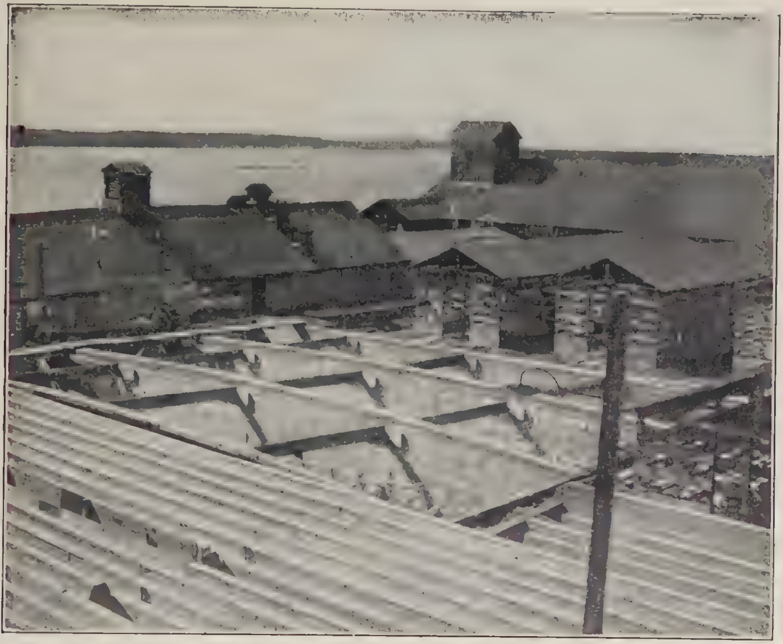

FIG. 99.—View showing portion of sand-troughs, settling-tanks, and drying-racks at a kaolin-washing plant. (After Ries, Md. Geol. Surv., IV, p. 270, 1902.)

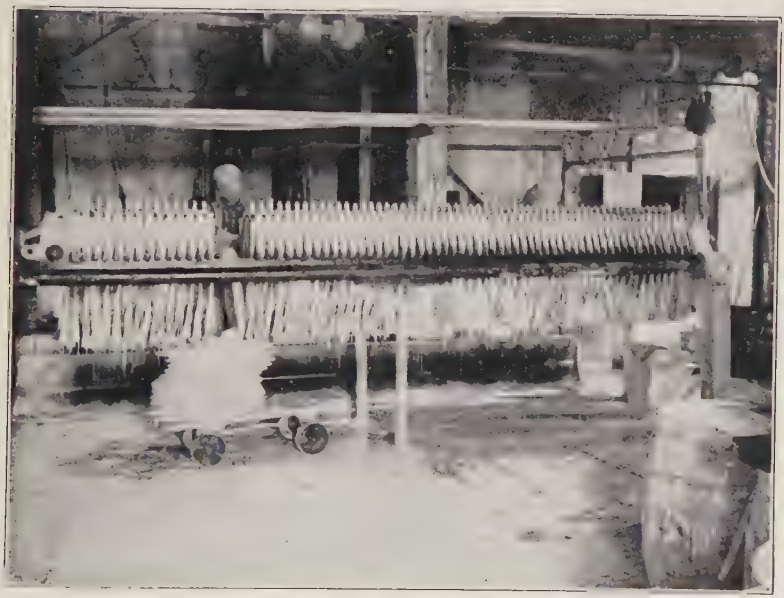

FIG. 100.—Filter-press for removing water from washed or blunged clays. The portion at the left end has been emptied and the leaves of clay taken from it are on the car. The workman is just removing a leaf of clay from the press. (After Ries, N. Y. State Mus., Bull. 35, p. 792, 1900.)

pumped into filter presses, to force out most of the water. After drying the clay is shipped to market.[1]

Most of the domestic supply of residual kaolin is obtained from western North Carolina, while smaller amounts come from Pennsylvania, Virginia, and Idaho.[2] Some has been produced in Canada, near Huberdeau in Quebec.

Chemical composition.—The analyses given below of both native and foreign residual kaolins, will give some idea of their composition. All of these are washed samples with the exception of No. I. A comparison of analyses I and II will therefore show the beneficial effects of washing.

ANALYSES OF RESIDUAL KAOLINS

	I	II	III	IV	V	VI
Silica (SiO_2)	62.40	45.78	46.28	73.80	46.50	72.30
Alumina (Al_2O_3)	26.51	36.46	36.25	17.30	37.40	18.94
Ferric oxide (Fe_2O_3)	1.14	.28	1.644	.35	.80	.40
Ferrous oxide (FeO)	....	1.08	....	....	....	....
Lime (CaO)	.57	.50	.192	....	tr.	.68
Magnesia (MgO)	.01	.04	.321	1.18	....	.39
Potash (K_2O)	.98	.25	1.69	2.49	1.1	.42
Soda (Na_2O)			.85	.20		
Titanium oxide (TiO_2)	....	....	....	....	....	....
Water (H_2O)	8.80	13.40	13.535	4.69	12.49	7.04
Moisture	.25	2.05	....	....	....	....
Total	100.66	99.84	100.762	100.01	98.29	99.57

I. Webster, N. C. Crude kaolin. N. C. Geol. Surv., Bull. 13, p. 62, 1897.
II. Webster, N. C. Washed kaolin. Ibid.
III. Brandywine Summit, Pa. Hopkins, Pa. State Coll., App. Rept., 1898–99, p. 36.
IV. Upper Mill, Pa. T. C. Hopkins, Ann. Rept., Pa. State Coll., 1899–1900, p. 11.
V. West Cornwall, Conn. H. Ries, analyst.
VI. Glen Allen, Mo. Mo. Geol. Surv., XI, p. 562, 1896.

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[1] See Watts, A. S., Mining and treatment of feldspar and kaolin in southern Appalachian region, U. S. Bur. Mines, Bull. 53, 1915; Sproat, I. E., Refining and utilization of Georgia kaolins, ibid., Bull. 128, 1916; Stull, R. T., and Bole, G. A., Beneficiation and utilization of Georgia Clays, ibid., Bull. 252, 1926.

[2] For descriptions of deposits see under those states.

Analyses of Residual Kaolins—*continued*

	VII	VIII	IX	X	XI
Silica (SiO_2)	45.44	43.31	48.26	46.87	47.71
Alumina (Al_2O_3)	40.30	39.42	37.64	38.00	36.78
Ferric oxide (Fe_2O_3)	.54	2.86	.46	.89	....
Ferrous oxide (FeO)	....	....	....	....	....
Lime (CaO)	tr.	.44	....	tr.	....
Magnesia (MgO)	tr.	.05	.04	.35	....
Potash (K_2O)	tr.	1.80	.25	1.22	2.58
Soda (Na_2O)	.38	.20	.30		
Titanium oxide (TiO_2)	....	.28	....	....	....
Water (H_2O)	13.9	10.26	12.02	13.58	13.03
Moisture	....	....	....	....	....
Total	100.56	99.96	100.00	100.03	100.10

VII. Leaky, Edwards County, Texas. O. H. Palm, analyst.
VIII. Crude kaolin, Cold Spring, Va. Analyzed by Va. Geol. Surv.
IX. Cornwall, Eng.
X. Zettlitz, Bohemia
XI. Coussac-Bonneval, France
U. S. Geol. Surv., Prof. Pap, 11, p. 39, 1903.

The following physical tests of crude and washed kaolin from Sprucepine, N. C., were made at the U. S. Bureau Mines Station at Columbus, O.[1]

General Physical Tests of Crude Kaolin from Opening of Sprucepine Mine, Half a Mile East-southeast of Sprucepine, Mitchell County, N. C.

Workability: very sandy; no strength; corners tear. Color of unfired clay: white.

	Per cent
Water of plasticity, in terms of dry clay	36.69
Air shrinkage by volume, in terms of dry clay	16.01
Air shrinkage, linear, calculated	5.7
Moisture factor on dry basis	1.317
Fineness test:	
Residue, 20-mesh sieve	21.58
Residue, 65-mesh sieve	17.39
Residue, 100-mesh sieve	1.16
Residue, 200-mesh sieve	1.95
Amount passing 200-mesh sieve	57.95

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[1] From U. S. Geol. Surv., Bull. 708, 1922.

FIRE TESTS OF KAOLIN FROM OPENING OF SPRUCEPINE MINE, HALF A MILE EAST-SOUTHEAST OF SPRUCEPINE, MITCHELL COUNTY, N. C.

Temperature (° C.)	Porosity (per cent in terms of burned volume)	Volume shrinkage (per cent in terms of volume of dry clay)
1190	35.7	14.7
1250	37.2	15.8
1310	36.0	16.8
1370	30.0	23.25
1410	18.7	27.6

GENERAL PHYSICAL TESTS OF WASHED KAOLIN, FROM SPARKS PLANT, SPRUCEPINE, MITCHELL COUNTY, N. C.

Workability: short, sandy; corners tear; dries well (no cracks); color of unfired clay: white.

	Per cent
Water of plasticity, in terms of dry clay	44.48
Air shrinkage by volume, in terms of dry clay	20.20
Air shrinkage, linear, calculated	7.3
Moisture factor on dry basis	.352
Fineness test:	
Residue, 20-mesh sieve	.00
Residue, 65-mesh sieve	.00
Residue, 100-mesh sieve	.00
Residue, 200-mesh sieve	2.92
Amount passing 200-mesh sieve	97.08

FIRE TESTS OF KAOLIN FROM SPARKS PLANT, SPRUCEPINE, MITCHELL COUNTY, N. C.

Temperature (° C.)	Porosity (per cent in terms of burned volume)	Volume shrinkage (per cent in terms of volume of dry clay)
1190	39.6	18.1
1250	39.7	18.4
1310	37.97	20.3
1370	35.5	24.98
1410	28.5	28.0

Uses.—The North Carolina kaolins are used chiefly in the manufacture of white wares, such as china, semi-porcelain, porcelain, floor tile, wall tile, and electrical porcelain. They have also been used in glass pots. The South Mountain and Saylorsburg, Pa., kaolins have been employed in their crude form in the manufacture of white Portland cement, while the washed product has been sold as a filler for paint, as well as for use in plaster board manufacture. Kaolin from Cold Spring, Va., is used in paper, paint and rubber manufacture.

Sedimentary kaolins.—Under this heading are included the white sedimentary clays of Georgia, South Carolina and Florida. Those from the first two are somewhat similar, while the last has appreciably greater plasticity, strength and shrinkage. All three are of considerable importance to a number of industries. Tests of these materials are given below, all being made by the Bureau of Mines at Columbus, Ohio.[1]

General Physical Tests of Sample of Clay from Pit of South Carolina Clay Co., at Langley, S. C.

Workability: fairly fat; makes good bars; dries fairly well.

	Per cent
Water of Plasticity, in terms of dry clay	39.61
Air shrinkage, by volume	15.83
Air shrinkage, linear, calculated	5.60

Fire Tests of Sample of Clay from Pit of South Carolina Clay Co., Langley, S. C.

Temperature (° C.)	Porosity (per cent in terms of volume of burned clay)	Color	Volume shrinkage (per cent in terms of volume of dry clay)	Linear shrinkage, calculated (per cent)
1190	38.17	White	22.21	8.1
1250	34.20	White	27.00	10.0
1310	32.67	White	32.20	12.2
1370	24.25	White	36.87	14.2
1410	12.50	White	44.20	17.7

Cone of fusion, 34.

A sample of this clay was used in a porcelain body and gave the results noted on p. 324.

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[1] U. S. Geol. Surv., Bull. 708, 1922.

GENERAL PHYSICAL TESTS OF PORCELAIN BODY CONTAINING CLAY FROM PIT OF SOUTH CAROLINA CLAY CO., LANGLEY, S. C.

Workability: plastic; molded well; fair jiggering body; good drying qualities.

	Per cent
Water of plasticity, in terms of dry clay	33.95
Volume shrinkage	22.60
Air shrinkage, linear, calculated	8.20
Modulus of rupture . . . . Pounds per square inch,	167.30

FIRE TESTS OF PORCELAIN BODY CONTAINING CLAY FROM PIT OF SOUTH CAROLINA CLAY CO., LANGLEY, S. C.

Temperature (° C.)	Porosity (per cent in terms of volume of burned clay)	Color	Volume shrinkage (per cent in terms of volume of dry clay)	Linear shrinkage, calculated (per cent)	Modulus of rupture (pounds per square inch)
1190	25.60	White	20.10	7.2	3323
1250	24.03	White	21.43	7.7	3709
1310	18.68	White	22.88	8.3	3881
1370	1.01	White	33.90	12.9	7788
1410	0.10	Light pale olive-gray	35.30	13.6	7383

GENERAL PHYSICAL TESTS OF CLAY FROM PIT OF GOLDING SONS CO., NEAR BUTLER, GA.

Workability: plastic; makes good bars.

	Per cent
Water of plasticity, in terms of dry clay	44.3
Air shrinkage by volume	20.38
Air shrinkage, linear, calculated	7.3

FIRE TESTS OF CLAY FROM PIT OF GOLDING SONS CO., NEAR BUTLER, GA.

Temperature (° C.)	Porosity (per cent in terms of volume of burned clay)	Color	Volume shrinkage (per cent in terms of volume of dry clay)	Linear shrinkage, calculated (per cent)
1190	40.20	White	21.45	7.8
1250	39.30	White	25.60	9.4
1310	36.70	White	28.08	10.4
1370	27.97	White	37.15	14.4
1410	17.80	White	41.80	16.5

Cone of fusion, 33½.

A sample of this clay was used in a porcelain body and gave the results noted below:

GENERAL PHYSICAL TESTS OF PORCELAIN BODY CONTAINING CLAY FROM PIT OF GOLDING SONS CO., NEAR BUTLER, GA.

Workability: plastic; makes excellent bars; jiggers well; dries well.

Water of plasticity, in terms of dry clay.....Per cent 31.54

Modulus of rupture.........Pounds per square inch, 132.6

FIRE TESTS OF PORCELAIN BODY CONTAINING CLAY FROM PIT OF GOLDING SONS CO., NEAR BUTLER, GA.

Temperature (° C.)	Porosity (per cent in terms of volume of burned clay)	Color	Volume shrinkage (per cent in terms of volume of dry clay)	Linear shrinkage, calculated (per cent)	Modulus of rupture (pounds per square inch)
1190	27.80	White..............	18.50	6.6	2621
1250	25.54	White; slight buff tint	22.59	8.2	2418
1310	23.15	White; slight buff tint	22.20	8.1	3995
1370	6.09	White..............	31.10	11.7	4815
1410	0.18	Pale smoke-gray.....	35.60	13.7	8203

GENERAL PHYSICAL TESTS OF WASHED CLAY FROM OKAHUMPKA, FLA.

Workability: very plastic; molds well.

	Per cent
Water of plasticity, in terms of dry clay............	49.78
Air shrinkage by volume........................	32.15
Air shrinkage, linear, calculated..................	12.20
Modulus of rupture........Pounds per square inch,	181.00

FIRE TESTS OF CLAY FROM OKAHUMPKA, FLA.

Temperature (° C.)	Porosity (per cent)	Color	Volume shrinkage (per cent in terms of dry clay)	Linear shrinkage (per cent in terms of dry clay)
1190	28.3	White..............	32.1	12.1
1250	27.05	Faint cream-white...	33.11	12.5
1310	23.41	Faint cream-white...	37.33	14.4
1370	7.4	Cream.............	46.3	18.7
1410	2.2	Buff...............	49.4	20.3

Deformation temperature, cone 31 + (1750° C.). Steel hard at 1190° C. Develops small cracks in firing.

A large portion of these sedimentary kaolins are washed before shipment to market.

A somewhat detailed study of the Georgia sedimentary kaolins by the U. S. Bureau of Mines[1] shows that after washing they can be used more in white ware than they are now, and to some extent in place of English china-clay in floor and wall tile. If mixed with grog made from the same clay, they yield a high grade refractory. Light-cream and light-gray face-brick can be made of a mixture of the Georgia white clay, aplite and sand.

Of the South Carolina clays the cream-colored grade is employed for filler in certain kinds of cheap textiles, cardboard, and paper, in the manufacture of colored hardware porcelain, in certain grades of electrical porcelain, in top printing wall paper, and in cold water paints. It is also employed as a filler in rubber goods, in oilcloth, and in the manufacture of certain kinds of patent roofing.

The white varieties are used for all purposes enumerated above and also for filling print, book, and magazine paper and white cotton goods, for coating paper and card-board, for coating and top printing wall paper in light shades, for making white and light-colored kalsomine, semi-porcelain, china, whiteware, and vitreous floor tiling.[2]

Florida white clay is extensively used in the manufacture of whiteware, electrical porcelain, and floor and wall tile. It is not usually regarded as a paper clay.

BALL-CLAYS

The term ball-clay is applied to those possessing good plasticity, usually strong bonding power, high refractoriness, and which burn white or creamy white. They are used chiefly in making white earthenware, and porcelain, but are also employed in floor and wall tile, and electric porcelain. Some are employed in the manufacture of glass refractories and graphite crucibles. In former years ball-clay for domestic use was obtained chiefly from England, but considerable quantities are now dug in western Tennessee and Kentucky. A small quantity is obtained in New Jersey. The English clay vitrifies at a lower temperature than the American material.

Analyses and tests of several ball-clays are given on pp. 327–329.[3]

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[1] U. S. Bur. Mines, Bull. 252, 1926.

[2] Bayley, U. S. Geol. Surv., Bull. 708, p. 187, 1922.

[3] All from U. S. Geol. Surv., Bull. 708, p. 1922; for comparison of English and American ball clays see, Sortwell, H. H., U. S. Bur. Stand., Tech. Pap. 227, 1923; Schroeder and Parmelee, Ball-clays of western Tennessee, Res. Tenn., IX, No. 2, 1919.

ANALYSES OF BALL CLAYS

	I	II	III
Silica (SiO_2)	46.85	48.99	46.87
Alumina (Al_2O_3)	33.15	32.11	36.58
Ferric oxide (Fe_2O_3)	2.04	....	1.14
Ferrous oxide (FeO)	....	2.34	....
Titanic oxide (TiO_2)	....	....	.43
Lime (CaO)	.35	.43	.50
Magnesia (MgO)	.40	.22	Trace
Potash (K_2O)	.61	3.31	Trace
Soda (Na_2O)	.10		1.60
Sulphur trioxide (SO_3)	.03	....	.06
Loss on ignition	16.45	9.63	11.52
Moisture at 100° C.	....	....	1.60
	99.98	97.03	100.30

I. Whitlock, Tenn. II. England. III. Mayfield, Ky.

GENERAL PHYSICAL TESTS OF TENNESSEE BALL CLAY NO. 11

Working property: good; sticky.	Per cent
Water of plasticity	42.5
Modulus of rupture:	Pounds per square inch
Raw clay	95.3
Mixture of clay and sand in proportion of 1 : 1	118.6
Slaking test, 9 minutes	
Fineness test:	
Residue, 20-mesh sieve	None
Residue, 40-mesh sieve	None
Residue, 60-mesh sieve	None
Residue, 80-mesh sieve	None
Residue, 120-mesh sieve	Trace
Residue, 150-mesh sieve	Trace
Residue, 200-mesh sieve	Trace
Drying shrinkage, linear.....per cent	5.75

	Color	Hardness	Total shrinkage (per cent)	Porosity (per cent)
Cone 2 (1170° C.)	White	Steel hard	21.5	21.15
Cone 5 (1200° C.)	White	Steel hard	16.3	19.6
Cone 9 (1310° C.)	Gray-white	Steel hard	17.2	17.7
Cone 12 (1370° C.)	Gray	Steel hard	17.8	2.2
Cone 13 (1390° C.)	....	Steel hard	17.5	3.4

Fusion test: Deformed at cones 32–33 (1770°–1790° C.).

The strength of this clay appears to be rather low. The color is very good and it is fairly well vitrified at cone 9 (1310° C.). It is fairly representative of the ball-clay type and will find use as a ball-clay. It will also be useful in the manufacture of sanitary ware, chemical and other stoneware, face brick, terra-cotta, and saggers. Its rather high fusion-point is likely to make it of service in the manufacture of refractories, where a plastic clay of good strength is desired.

General Physical Tests of Clay No. 3, Kentucky Construction & Improvement Co., Pryorsburg, Ky.

Workability: very plastic, sticky; pulls under spatula.

	Per cent
Water of plasticity	41.72
Air shrinkage by volume	31.92
Air shrinkage, linear, calculated	12.00
Modulus of rupture:	Pounds per square inch
Raw clay	25.55
Mixture of clay and sand in proportion 1 : 1	196.30

Fire Tests of Clay No. 3, Kentucky Construction & Improvement Co., Pryorsburg, Ky.

Temperature (° C.)	Porosity (per cent)	Color	Volumetric shrinkage (per cent in terms of dry clay)	Linear shrinkage (per cent in terms of dry clay)
1190	16.70	Cream-colored	32.00	12.0
1250	16.79	Cream-colored	29.89	11.20
1310	1.59	Cream-colored	37.52	14.50
1370	.90	Brown-buff	40.00	15.60
1410	.30	Brown-buff	38.00	14.70

Fuses at cone 32 + (1770° C.+). Steel hard at 1190° C. At 1310° C. the clay shows small yellowish specks.

Tests of Some English Ball Clays *

Water plasticity per cent	39.9–51.9
Volume drying shrinkage per cent	21.9–29.5
Ratio pore water to shrinkage water	0.64–1.10
Bulk specific gravity, dry clay	1.413–1.753
Modulus of rupture, 1 flint : 1 clay, pounds per square inch	345–563

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* Sortwell, U. S. Bur. Stand., Tech. Pap. 227.

Cone	Apparent porosity, per cent	Volume shrinkage, per cent
01	1.8–26.2	24.0–35.5
2	1.0–15.4	25.8–40.4
4	0.7– 7.7	27.0–41.3
6	0.2– 3.9	29.5–42.9
8	0.2– 3.9	30.4–43.5
10	0.2– 3.6	30.4–44.2
12	0.3– 3.4	30.2–44.9

TESTS OF TENNESSEE BALL CLAYS *

Water plasticity	per cent	45–46
Modulus of rupture, dry clay	pounds per square inch	95–466
Modulus of rupture, 1 clay : 1 sand	pounds per square inch	61–232
Linear drying shrinkage	per cent	5.5–7.5

Slaking time, 7–14 minutes

Cone	Total linear shrinkage, per cent	Porosity per cent
2	10.3–21.5	21.2–33.7
5	12.6–16.3	10.4–19.6
9	13.1–17.3	2.2–17.3
12	....	0.26–4.0

Cone of fusion, 30–35.

* Parmelee, C. W., Res. Tenn., IX, No. 2, 1919.

REFRACTORY BOND CLAYS

In this group we may include those clays which in addition to their refractoriness have a strong bonding power, which makes them of value for glass refractories, for crucibles to melt steel and brass, and to a less extent for the bond of abrasive wheels. They are all fire-clays, and some ball-clays could be included here.

The properties of the clays in their raw condition and those developed in firing are both important.

The properties of the raw clays to be considered are their transverse strength, especially if mixed with an equal amount of sand, and the ratio of pore to shrinkage water. Bleininger and Loomis[1] suggest that clays may be divided into two classes—the first-class including those whose modulus of rupture is 325 lbs. per square inch or more, and those in which it is 225 to 325 lbs. The ratio of pore water to shrinkage water should not exceed 1.00 for clays of the first-class. For strong, heavy, plastic clays, low in free silica, the ratio should not exceed 0.75, but siliceous bond clays such as the Gross Almerode pot clay of Germany, cannot meet this requirement.

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[1] Trans. Amer. Ceram. Soc., XIX, p. 601, 1917; U. S. Bur. Stand., Tech. Pap. 144, 1920.

The principal criteria of the value of the clay, as determined by burning are the over-firing temperature and the softening point. For very severe service the clay should not develop a definite vesicular structure below 1425° C., nor a softening point below cone 31 (1750° C.); but, as Bleininger says, this specification may not be fair to some plastic clays that are of use in the manufacture of graphite crucibles, especially for brass melting, although even for this purpose the temperature of overfiring should not be much below 1400° C. and the softening temperature not much below that of cone 30 (1670° C.). Anything below these requirements is to be ruled out as a bond clay.

Bleininger suggests the following classification:

1. Clays particularly suited to manufacture of graphite crucibles used for melting brass. Should burn dense at 1150° C. and shown no evidence of overfiring at 1400° C. and have other required physical properties.

2. Clays adapted for crucibles for steel melting. Should burn dense around 1275° C., and not overfire at 1400° C., or higher.

2*a*. Clays like those of class 2 but that do not overfire below 1425° C. These clays are valuable in addition for glass refractories.

3. Clays especially suited to glass industries.[1] Should burn dense only at 1425° C. or even higher, and not overfire below 1450° C.

Clays that become dense between 1150° C. and 1300° C. and that overfire at or just above the temperature at which they become dense are of no value as refractory bond clays.

The table on p. 331 compiled from Bleininger and Loomis shows the characteristic physical properties of a number of good refractory bond clays as well as some that are deficient in refractoriness.

A number of interesting tests of crucible clays mixed with graphite have been made by M. C. Booze,[2] from which he concludes that no one clay satisfies to a high degree all the requirements for crucibles. Indeed,

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[1] See also Jenkinson, S. N., Jour. Soc. Glass Tech., II, p. 272, 1918; Rees, W. J., Trans. Ceram. Soc. (Eng.), XVIII, p. 420, 1919, and Jour. Amer. Ceram. Soc., III, p. 332, 1920.

[2] Jour. Amer. Ceram. Soc., II, p. 461, 1919. For other tests see Ill. Geol. Surv., Bull. 36, p. 73, 1916; U. S. Bur. Stand., Tech. Pap. 144, 1920.

PHYSICAL PROPERTIES OF SOME REFRACTORY BOND CLAYS

Water in terms of dry weight	Ratio of pore water to shrinkage water	Shrinkage by volume in terms of dry volume	Time of slaking, minutes	Modulus of rupture of dried clay in pounds per square inch	Modulus of rupture of dried mixture of 1 part clay to 1 part sand in pounds per square inch	Temperature of vitrification ° C.	Temperature of overfiring, ° C.	Remarks
44.90	0.79	43.30	30	376	323	1150	1320	English ball clay; not satisfactory for steel-melting crucibles or glass refractories. Brass crucibles?
39.68	.57	42.58	78	345	381	1125	1425	Klingenberg, A. T. Cracks badly when used alone. Useful for graphite crucibles but not for glass refractories.
31.23	.69	35.01	12	475	255	1200	1230	New Jersey. No value as a high-grade bond clay.
31.14	.57	38.42	52	838	399	1290	1320	St. Louis. No value as a high-grade bond clay
50.66	.56	55.05	108	230	363	1100	1400	Klingenberg, E. T. Good bond clay.
43.63	.72	43.63	33	328	351	1200	1430	St. Louis. Promising as a crucible material.
45.28	1.05	34.53	9	239	234	1260	1425	Kentucky. No good when used alone. Could be mixed with a stronger clay for crucibles, possibly glass.
22.08	.80	24.46	8	479	281	1350	1350+	Southern Ohio. Not highest type of bond clay. Somewhat deficient in bonding power. Used in mixture.
40.33	.75	39.85	41	366	389	1125	1415	English ball clay. Useful for crucibles. Desirable ingredient of glass-pot mixture.
37.65	1.05	31.01	5½	187	199	1260	1425	Tennessee. Low bonding power. Good firing range. Useful in mixture for steel or brass crucibles.
45.16	.65	45.35	54	439	341	1230	1450	Southern Illinois. Excellent for glass refractories or crucibles.
50.85	.71	46.80	36½	359	362	1290	1400	Kentucky. Good bond clay, especially for steel-melting crucibles or glass refractories.
38.91	.67	40.61	113½	667	518	1250	1350	Maryland. Probably suitable for crucibles.
29.02	.72	32.32	128	817	466	1450+	....	Arkansas. Excellent glass-pot clay. Not suitable for crucibles.
20.64	.99	20.57	49½	502	364	1450+	....	Gross Almerode. Good for glass refractories.
31.39	.81	31.36	55	645	326	1350	1450	Mississippi. A good bond clay.

some of these requirements are so diametrically opposite that no one clay is entirely satisfactory. By selecting the clays that rank higher than the others in all or most of the requisite properties, using them as a base, and blending them with others, it is possible to get a mixture that gives better results than any one clay alone would yield.

Booze tested twenty-one clays, the mixtures consisting of equal parts of clay and Alabama graphite. Results on the following six are given below:

No. 3.01, St. Louis, Mo.; No. 3.10, Pennsylvania fire-clay; No. 3.14, Enid, Miss.; No. 3.18, Mayfield, Ky.; No. 3.20, Dorset, Eng., ball-clay; No. 3.22, Klingenberg, Ger., bond clay.

Working qualities:

3.22. Warps considerably in drying	Very good working qualities.
3.20. Warps considerably in drying	
3.14. Warps somewhat	Good working qualities.
3.01. Warps somewhat	
3.18. Dries well	
3.10. Dries well. Too lean for molding.	

No trouble from cracking with any of the clays.

TESTS OF CRUCIBLE CLAYS

Number	Water plasticity	Dryshrinkage in terms of dry volume	Ratio pore to shrinkage water	Ratio pore to true volume of bar	Time of slaking, minutes
3.01	28.31	22.59	1.117	36.5	73
3.14	26.17	18.98	1.360	36.9	89
3.18	34.08	24.10	1.200	45.4	74.5
3.20	31.17	23.38	1.178	40.64	71.5
3.22	32.02	24.54	0.879	39.16	170

Number	Dry strength	Strength after burning to 800° C.	Strength after burning to 1425° C.	Strength after burning to 1425° C.	Strength after burning to 1150° C. and quenching 5 times
3.01	576.4	1104.11	1131.9	1308.8	768.31
3.14	510.9	956.3	1226.1	1459.5	727.7
3.18	431.9	644.0	1000.7	1080.0	569.9
3.20	464.5	846.0	1020.0	1234.5	640.1
3.22	691.7	1035.1	1219.5	......	......

Tests of Crucible Clays—*continued*

Number	Strength after burning to 1425° C. and quenching 5 times	Per cent loss in strength after burning at 1150° C. and quenching	Per cent loss in strength after burning at 1425° C. and quenching	Softening point in standard cones
3.01	1125.1	32.1	14.0	31
3.14	845.7	40.65	42.1	30½
3.18	749.6	43.1	30.6	33
3.20	724.8	37.2	41.3	33
3.22	526.4	56.8	....	31½

Number	Oxidation trials burned at 1150° C. Oxidized for 10 hours at 1100° C.			Oxidation trials burned at 1425° C. Oxidized for 10 hours at 1100° C.		
	Per cent of whole area oxidized	Per cent loss in weight	Per cent graphite burned out	Per cent of whole area oxidized	Per cent loss in weight	Per cent of graphite oxidized
3.01	94.40	31.53	62.0	70.14	42.2	83.0
3.14	51.67	32.50	63.3	71.87	49.14	96.6
3.18	70.53	42.23	83.0	75.76	46.21	90.75
3.20	53.43	32.93	64.7	50.0	36.96	72.6
3.22	40.94	29.86	58.7	....	......	......

Distribution of refractory bond clays.—The domestic supply of refractory bond clays is obtained chiefly from the Wilcox group of northwestern Mississippi and the Lagrange formations of western Tennessee and Kentucky, and southern Illinois. In addition the Carboniferous of the St. Louis, Mo., and the Portsmouth, Ohio, districts is of importance. Small amounts have been obtained from Alabama, New Jersey, and Maryland. The Wilcox clays near Lester, Ark., were at one time worked for glass pot material.

FIRE-CLAYS

The term fire-clay, properly speaking, refers to those clays capable of withstanding a high degree of heat, but it is unfortunately most loosely used by American clay-workers, and many plastic materials which have absolutely no claim to refractoriness are included under this head. It is to be greatly regretted that no standard of refractoriness has been adopted by producers and consumers of refractory clays in the United States, nor for that matter in Europe, although the term is probably less abused there than it is here. In the author's opinion no clay should be classed as a fire-clay unless its fusion-point is higher than that of cone 27.

In many parts of the United States it is common to grade both fire-clays and fire-bricks as No. 1 and No. 2, a practice which should be discouraged unless the term has some standardized meaning, which it lacks at the present time. Even in the same district a No. 1 clay or brick of one manufacturer may be no better than the No. 2 clay or brick of another manufacturer. It therefore seems reasonable to urge that unless the terms No. 1 and No. 2 refer to certain definite and accepted standards, they should be dropped, as they only lead to confusion.

One common misuse of the term *fire-clay* may also be referred to in this place. It is a prevalent custom in the United States to apply the term fire-clay to all clays or shales found underlying coal-beds. While it is true that in several States, such as Pennsylvania, Ohio, West Virginia and Kentucky, valuable fire-clays underlie the coals, still sometimes even in these States, and always in some others, as Michigan, clay or shale is found under the coal, which is not refractory by any means. There is at times nothing in the appearance of these underclays to tell whether they are refractory or not.

Aside from refractoriness, which is the most important property of a fire-clay and the one possessed by all true ones, they vary widely, showing great differences in plasticity, density, shrinkage, transverse strength, and color. The resistance of a fire-clay to heat is governed primarily by its chemical composition and secondarily by its texture.

Chemical composition.—Fire-clays contain practically all the substances usually determined by the ultimate analysis (p. 97), but in every good fire-clay the total percentage of certain fluxing impurities, such as ferric oxide, lime, magnesia, and alkalies, is small. This is necessarily the case, since, if the fluxing impurities were present in large quantities, the clay would fuse at comparatively low temperatures and could not be classed as refractory.

The influence of these different ingredients of a clay has been discussed on pp. 111–147.[1] It might be emphasized here again, however, that the chemical analysis is of restricted value as a means of interpreting the refractoriness of the clay, except insofar as this property is indicated by low total fluxes and low silica. The belief that high silica as compared with alumina, indicated high refractoriness is probably no longer as prevalent as it used to be.

Physical properties.—Texture is also an important factor in determining the refractoriness, and for this reason the author has always opposed fine grinding of either a fire-clay or fire-brick before its fusion-point is determined. A striking illustration of this is the case of certain New Jersey fire-brick, containing quartz in coarse grains, whose fusion-point was cone 33. According to the $SiO_2 : Al_2O_3$ ratio in them it should have been cone 26. When these brick were ground to 100-mesh, made up into cones and tested, the fusion-point dropped to cone 27.

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[1] Bales, C. E., Effect of impurities in fire clay, Jour. Inst. Metals, XXX, p. 699.

If there is little difference in composition between the fine and coarse particles, grinding up the sample before testing would make little difference.[1]

Classification of fire-clays.—There is not unanimity of opinion regarding the temperature dividing line between a refractory and non-refractory clay. Ries suggests the following:[2]

1. Highly refractory clays fusing above cone 33.
2. Refractory clays fusing from cone 31–33 inclusive.
3. Semi-refractory clays fusing between cones 27 and 30.
4. Clays of low refractoriness, fusing between cones 20 and 26.

Bleininger [3] believes that a No. 1 fire-clay should not soften below cone 31, and a No. 2 not below cone 28.

Purdy and Moore [4] attack the matter from a different view point. They classify clay according to changes in porosity and specific gravity curves at different temperatures. Thus:

No. 1 fire-clay shows small but regular decrease in porosity from the beginning of firing to above cone 11.

No. 2 fire-clay shows increase in the loss of porosity, and hence early vitrification, the change beginning about cone 04.

No. 3 fire-clay shows a marked change with increasing low porosity at cone 1, and fusion rarely above cone 16 or 17.

Uses of fire-clays.—It is but natural that all fire-clays are not adapted to the manufacture of all kinds of refractory wares. Of the latter some have to resist heat alone, others changes of temperature, resistance to abrasion or corrosion, etc. Consequently the aim of the manufacturer is to select a clay or mixture of clays which will give a body on firing, best adapted to the conditions under which it is to be used. To enumerate the qualities of a fire-clay needed for each type of refractory product, would be beyond the scope of this book. A number of articles have been published on this subject.[5]

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[1] Hofman, H. O., and Stoughton, B., Trans. Amer. Inst. Min. Engrs., XXVIII, p. 440, 1898.

[2] N. J. Geol. Surv., Fin. Rept., VI. 1904.

[3] Eng. Soc. West. Pa., XXXII, p. 613, 1916.

[4] Trans. Amer. Ceram. Soc., IX, p. 239, and Ill. Geol. Surv., Bull. 9, p. 270, 1908.

[5] See Bibliography of Literature on Refractories, Jour. Amer. Ceram. Soc., X, Feb., 1927, Pt. II; Fire-clay Brick, manufacture properties uses and specifications, U. S. Bur. Stand., Circ. 282, 1926.

The main use of fire-clays is for the manufacture of the various shapes of fire-brick, but in addition they are used wholly or in part in the manufacture of gas- and zinc-retorts, locomotive and furnace linings, crucibles, floor-tiles, terra-cotta, conduits, pressed and paving-bricks, coke oven brick, saggers, etc.

Reference should also be made to the Refractory Bond Clays mentioned on pp. 329–333.

Analyses of fire-clays.—The analyses given on pp. 336–337 show the composition of a number of fire-clays from various localities in the United States, and for additional ones reference should be made to the State descriptions.

ANALYSES OF FIRE-CLAYS

	I	II	III	IV	V	VI
Silica (SiO_2)	74.25	63.00	52.52	59.92	62.89	51.92
Alumina (Al_2O_3)	17.25	23.57	31.84	27.56	21.49	31.64
Ferric oxide (Fe_2O_3)	1.19	.46	.67	1.03	....	....
Ferrous oxide (FeO)	....	1.87	....	....	1.81	1.13
Lime (CaO)	.40	.44	.50	tr.	.38	.03
Magnesia (MgO)	tr.	.89	.19	tr.	.56	.44
Potash (K_2O)	.52	2.40	.59	.67	2.52	.40
Soda (Na_2O)		.29				
Sulphur trioxide (SO_3)	....	....	....	....	....	....
Titanic acid (TiO_2)	....	1.10	1.68	....	1.82	1.16
Water (H_2O)	6.30	6.45	11.68	9.70	7.58	13.49
Moisture	....	....	....	....	1.16	....
Total	99.91	100.47	99.67	98.88	100.21	100.21

	VII	VIII	IX	X	XI	XII
Silica (SiO_2)	51.56	46.56	59.36	61.44	73.00	50.35
Alumina (Al_2O_3)	33.13	37.47	23.26	26.18	15.79	33.64
Ferric oxide (Fe_2O_3)	.78	tr.	3.06	.30	.63	.75
Ferrous oxide (FeO)	....	....	....	.36	....	....
Lime (CaO)	tr.	.112	.65	.12	1.29	....
Magnesia (MgO)	tr.	tr.	.42	....	1.53	tr.
Potash (K_2O)	tr.	.28	.63	.....	.10	.49
Soda (Na_2O)	tr.	.28		.02	.16	.09
Sulphur trioxide (SO_3)	....	....	.35	....	....	....
Titanic acid (TiO_2)	1.91	....	1.01	1.39	.43	.80
Water (H_2O)	12.50	13.03	10.20	9.07	5.76	11.75
Moisture			2.74	.77	....	2.13
Total	99.88	97.732	101.68	99.65	98.69	100.00

Analyses of Fire-clays—*Continued*

	XIII	XIV	XV	XVI	XVII
Silica (SiO_2)	40.28	54.80	44.16	39.56	73.20
Alumina (Al_2O_3)	34.72	29.44	37.44	43.35	18.56
Ferric oxide (Fe_2O_3)	.84	1.70	1.28	2.57	.50
Lime (CaO)	.05	....	.25	.56	.29
Magnesia (MgO)	.04	....	tr.	.50	.52
Potash (K_2O)	tr.	....	.53	....	.36
Soda (Na_2O)	....	....		....	.38
Sulphur trioxide (SO_3)	tr.	....	.31	....	....
Titanic acid (TiO_2)	1.15	.82	tr.	....	....
Water (H_2O)	12.39	8.84	14.60	13.09	5.93
Moisture	10.72	2.37	2.82	....	....
Total	100.19	97.97	101.29	99.63	99.74

I. Bibbville, Ala. Ala. Geol. Surv., Bull. 6, p. 152, 1900.
II. Mecca, Parke County, Ind. Ind. Dept. Geol. and Nat. Res., 29th Ann. Rept., p. 507, 1905.
III. Mineral Point, O. (Flint-clay). Mo. Geol. Surv., XI, p. 591, 1896.
IV. Salineville, O. (Flint-clay). Ohio Geol. Surv., VII, p. 221, 1893.
V. Lower Kittanning clay, New Brighton, Pa., 2d Pa. Geol. Surv., MM, p. 262.
VI. Bolivar flint fire-clay, Salina, Pa. Ibid., p. 259.
VII. Woodbridge, N. J. No. 1 fire-clay, N. J. Geol. Surv., VI, p. 441, 1904.
VIII. Boone Furnace, Ky. Coal measures, U. S. Geol. Surv., Prof. Pap, 11, p. 119.
IX. St. Louis, Mo. Mo. Geol. Surv., XI, p. 571, 1896.
X. Piedmont, W. Va. Mount Savage clay, W. Va. Geol. Surv., III.
XI. Athens, Tex. O. H. Palm, analyst.
XII. Golden, Colo. U. S. Geol. Surv., Mon. XXVII, p. 390.
XIII. Dry Branch, Ga. U. S. Geol. Surv., Bull. 315, p. 303, 1907.
XIV. Coal-measures clay, Utica, Ill. Ill. Geol. Surv., Bull. 4.
XV. White clay, Subcarboniferous, 5 m. s. e. Bonnieville, Ky. Ky. Geol. Surv., Bull. 6.
XVI. "Aluminite," Olive Hill, Ky., Carboniferous. Trans. Amer. Ceram. Soc., IX, p. 461, 1907.
XVII. White siliceous Tertiary clay, N. Dak. 4th Bien. Rept., Dak. Geol. Surv.

Physical properties.[1]—The range in physical properties exhibited by a number of fire-clays from different localities is as follows:

Tests of Fire-clays

	Plastic	Flint
Water plasticity	12.9–37.4	8.89–19.04
Volume air shrinkage	6.67–28.80	2.36–21.12
Linear air shrinkage	1.7–9.4	0.78–6.59
Tensile strength dried	41–65	....

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[1] For further information see reports on those states containing fire-clays.

TESTS OF SOME MARYLAND PLASTIC FIRE-CLAYS SUITABLE FOR NO. 1 FIRE-BRICK

Temp., ° C.	Apparent porosity, per cent	Apparent specific gravity	Volume shrinkage, per cent
1150	4.6–24.9	2.46–2.67	15.7–34.1
1200	2.3–23.0	2.39–2.67	18.7–36.0
1250	1.3–23.8	2.36–2.68	22.2–37.4
1275	0.9–21.9	2.35–2.65	23.0–36.5
1300	0.5–22.1	2.35–2.64	22.6–36.1
1325	1.1–20.4	2.35–2.61	22.4–35.5
1350	0.8–20.0	2.33–2.61	25.3–35.7
1375	1.4–18.7	2.30–2.60	24.5–34.5
1400	2.0–18.9	2.23–2.61	23.9–33.3

Softening point, cones 31–32.

TESTS OF MARYLAND FLINT CLAYS FOR NO. 1 FIRE-BRICK *

Temp., ° C.	Apparent porosity, per cent	Apparent specific gravity	Volume shrinkage, per cent
1150	25.0–40.0	2.02–2.74	8.6–17.9
1200	26.0–41.0	2.00–2.74	8.2–19.7
1250	26.7–41.3	2.08–2.73	9.8–18.9
1275	24.8–43.2	2.09–2.74	8.0–18.6
1300	25.2–43.8	2.11–2.73	7.6–18.6
1325	23.7–45.6	2.12–2.70	7.3–17.6
1350	24.3–43.2	2.06–2.70	6.6–16.8
1375	25.0–44.2	2.03–2.70	4.51–16.3
1400	24.8–47.1	2.04–2.64	3.2–15.7

* From Md. Geol. Surv., vol. XI, Pt. II.

Occurrence and distribution.—Fire-clays may be of either residual or sedimentary origin, and of the two the latter are by far the more important commercially. This class is further subdivisible into plastic fire-clays and flint-clays. The former are plastic when wet, the latter are hard and flint-like, with a smooth, shell-like fracture and dense texture. They develop but little plasticity, even when ground fine, but are usually highly refractory. Flint-clays are found at a number of points in the Carboniferous of Pennsylvania, Ohio, Maryland, Kentucky, and West Virginia, where they occur often underlying coal-seams and in the same bed with the plastic clay, the two showing no regularity of arrangement, and often differing but little if at all in chemical composition. They are also known in the Cretaceous of Georgia, the Tertiary of Alabama, and the Cretaceous of Colorado. Their peculiar character has been a puzzling problem to geologists, but it seems probable that they may have been formed by a solution and reprecipitation of the clay by percolating water subsequent to its formation. A second type of flint-clay is that found occupying basins in Paleozoic limestones in Missouri (which see). Some flint-clays show a higher alumina content than is required for kaolinite, and they are thought to contain pholerite. Others may carry diaspore (Missouri) or gibbsite (Kentucky).

In many States [1] fire-clays are often found underlying coal-beds, and on this account it has been suggested that their alkalies and other fluxing impurities have been abstracted by the roots of plants which grew in the swamps in which these clays were deposited, while the decay of these plants later gave rise to the coal-bed overlying the clay. This theory seems rather improbable, as in some States, such as Michigan and Alabama, the clays and shales underlying the coals always contain sufficient impurities to render them non-refractory. Furthermore, the extensive beds of refractory clay, found in the Tertiary-Cretaceous formations of the Atlantic and Gulf coastal plains, are very rarely associated with coal-beds.[2]

We must, therefore, assume that these clays were either derived from rocks running low in fusible impurities, or else that these were removed by solution during the transportation and deposition of the clay particles.

In the United States fire-clays are widely distributed, both geologically and geographically. The most important occurrences are in the Carboniferous of Ohio, Pennsylvania, Kentucky, Indiana, Illinois, Maryland, West Virginia, and Missouri. Many other deposits are, however, found in the Cretaceous of New Jersey, Maryland, Georgia, South Carolina, Alabama, Texas, Iowa, Colorado, South Dakota, etc., and in the Tertiary of New Jersey, Georgia, South Carolina, Alabama, Texas, Arkansas, and California.

The clays near Lester, Ark., which occur in the Wilcox formation were also worked at one time. Some have been obtained from the Woodbridge district of New Jersey.

In Canada the most extensive deposits of refractory clay occur in southern Saskatchewan, and southwestern British Columbia.

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[1] Ohio, Pennsylvania, Kentucky, Indiana, and West Virginia.

[2] See Coal-measures fire-clays, p. 29.

Sagger-clays

Saggers are containers in which white wares or other clay products are placed in firing to protect them from the gases and dirt of the kiln. They are usually made of a mixture of clays, most of which are of refractory character.

A mixture employed[1] consists of a vitrifying bond clay, an open burning clay and grog. Excess of the first may make the sagger sensitive to temperature changes, but a deficiency causes weakness. The mixture should have good strength in its dry condition, and be free from iron or granular materials liable to cause spitting or popping out. A small addition of kaolin or similar open-burning clay is sometimes beneficial. The real value of a sagger mixture lies in its life when repeatedly used. They are rarely exposed to a temperature of over cone 13.

Bleininger[2] classifies sagger clays as follows: (1) Those having a drying-shrinkage of 7 per cent and a fire-shrinkage at cone 8 of 5.5 per cent; absorption at cone 8 of 2.5 per cent, transverse strength dry, 120 lbs. per square inch. They have good strength in the first fire but overburn gradually and sometimes soften in subsequent firings; (2) drying shrinkage, 6.2 per cent; fire-shrinkage, 3.4 per cent; absorption at cone 8 is 12 per cent; dry strength, 120 lbs. per square inch; (3) drying shrinkage, 7 per cent; fire-shrinkage, 6.8 per cent; absorption, 2.3 per cent; dry strength, 220 lbs. per square inch. Do not shrink or overfire in repeated firings. (4) Drying shrinkage, 4 per cent; fire-shrinkage, 4 per cent; absorption at cone 8, 15 per cent; dry strength, 80 lbs. per square inch; quite high in silica and do not overfire. Clays 1, 2 and 3 are said to give the best results.[3]

The following figures give the results of physical tests on fifty-one sagger clays by Heindl:

Physical Tests of Sagger Clays

Water plasticity	per cent	13.7–31.7,	av. 19.5
Volume air shrinkage	per cent	9.1–16.9,	av. 13.1
Linear air shrinkage	per cent	2.8–6.1,	av. 4.5
Porosity dried	per cent	24.4–50,	av. 31.9
Modulus of rupture, dry, pounds per square inch		46.0–386,	av. 221
Softening point, cone		14+–30	

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[1] Brown, G. H., Jour. Amer. Ceram. Soc., I, p. 716, 1918.

[2] Brick and Clay Record, LX, p. 39, 1922.

[3] See also: Moore, B. J., Trans. Ceram. Soc. (Eng.), XX, p. 93, 1921; Heindl, R. A., Jour. Amer. Ceram. Soc., IX, p. 131, 1926; Geller, R. F., and Heindl, R. A., ibid., IX, p. 555, 1926; Searles, Refractory Materials, Their Manufacture and Uses, 2nd ed., 1924, p. 442; Twells, R., Jr., Jour. Amer. Ceram. Soc., VI, p. 949, 1923.

Range in Modulus of Rupture of Fired Sagger Clays

Temp., ° C.	Minimum	Maximum	Average
1110	405	3850	2600
1150	500	4340	1880
1180	510	4340	2030
1230	620	5350	2320
1270	610	4850	2590
1310	755	4960	2760

Range in Porosity and Volume Shrinkage of Sagger Clays

Temp., ° C.	Porosity			Volume shrinkage		
	Minimum	Maximum	Average	Minimum	Maximum	Average
1110	18.0	23.5	19.9	2.2	14.9	10.0
1150	17.4	46.5	31.1	1.9	16.3	7.6
1180	13.9	45.9	30.8	2.7	18.2	8.3
1230	8.1	40.8	27.1	4.0	24.7	11.0
1270	1.0	38.5	22.5	2.1	35.7	14.3
1310	8.8	39.2	25.0	2.5	30.2	11.0

Stoneware-clays

Physical properties.—Stoneware is usually made from a refractory or semi-refractory clay, but at some small potteries a much lower grade of material is used. While the material is often as refractory as a clay used for fire-brick, it differs from it in burning to a very dense body at a comparatively low temperature. It should have sufficient plasticity and toughness to permit its being turned on a potter's wheel; good bonding strength, rather long firing range, low air- and fire-shrinkage, and yet sufficient refractoriness to make the ware hold its shape in burning. Concretionary minerals, such as iron or lime, which are liable to cause blisters, should be avoided. Most stoneware is now made from a mixture of clays, so as to produce a body of the proper qualities, both before and after burning.

For the manufacture of chemical stoneware great care is necessary in the selection of the raw materials, and a mixture of three or four clays may sometimes be used.

The following analyses give the composition of stoneware clays from a number of different localities:

ANALYSES OF STONEWARE CLAYS

	I	II	III	IV	V	VI	VII	VIII
Silica (SiO_2)	67.10	71.94	67.84	57.20	64.26	68.3	60.34	69.23
Alumina (Al_2O_3)	19.37	17.60	21.83	24.82	22.95	20.1	20.55	18.97
Ferric oxide (Fe_2O_3)	2.88	2.35	1.57	3.25	1.28	1.0	3.53	1.57
Ferrous oxide (FeO)	......	......	......	1.42	......	tr.	.49	.55
Lime (CaO)	tr.	.62	.28	.73	.45	tr.	.38	.12
Magnesia (MgO)	.725	.56	.24	.13	.37	2.4	1.12	.36
Potash (K_2O)	.672	1.50	2.24	.93	1.96	tr.	2.89	2.27
Soda (Na_2O)	......	......	......	......	......	.6	.73	.33
Titanic acid (TiO_2)	......	......	......	......	......	1.2	.92	1.5
Water (H_2O)	6.08	5.27	5.9	8.25	6.74	6.6	6.42	5.46
Moisture	1.71	1.01	.8	2.10	2.05	......	2.35	......
Phosphorous acid (P_2O_5)	......	......	......	......	......	......	.55	......
Total	98.537	100.85	100.70	97.83	100.06	100.20	100.27	100.37

I. Thirteen miles from Fayette C. H., Fayette County, Ala. Ala. Geol. Surv., Bull. 6, p. 176, 1900.
II. Calhoun, Henry County, Mo. Mo. Geol. Surv., XI, p. 564, 1896.
III. Woodbridge, Middlesex County, N. J. N. J. Clay Rept., 1878, p. 99.
IV. Lincolnton, N. C. N. C. Geol. Surv., Bull., 13, p. 78, 1897.
V. Akron, Summit County, O. Ohio Geol. Surv., VII, p. 94, 1893.
VI. Elmendorf, Bexar County, Tex. O. H. Palm, analyst.
VII. Bridgeport, Harrison County, W. Va. W. Va. Geol. Surv., III, p. 162, 1906.
VIII. Huntingburg, Ind. Ind. Dept. Geol. and Nat. Res., 29th Ann. Rept., p. 508, 1904.

The following data give the physical properties of nine stoneware clays from the Carboniferous of Ohio and Pennsylvania.[1] The samples were all washed through a 150-mesh sieve:

PHYSICAL PROPERTIES OF STONEWARE CLAYS

RAW CLAY

Porosity, per cent	25.6 – 29.7
Modulus of rupture, pounds per square inch	191.0 –499.2
Per cent total water in terms of true clay volume	37.1 – 55.6
Per cent shrinkage water in terms of true clay volume	34.0 – 45.0
Ratio percentage pore water to percentage shrinkage water	0.61– 11.6
Water plasticity in terms of dry weight	28.9 – 34.8
Volume air shrinkage	26.4 – 41.2

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[1] Schurecht, H. G., U. S. Bur. Mines, Tech. Pap. 233; and Jour. Amer. Ceram. Soc., I, p. 267, 1918.

FIRED CLAY

Modulus of rupture, pounds per square inch	Cone 6	4,666–10,448
	Cone 8	4,820– 8,680
	Cone 10	2,716– 7,505
Apparent porosity, per cent	Cone 01	17.58–26.75
	Cone 4	0.14–17.50
	Cone 8	0.08– 5.23
	Cone 12	0.17– 8.80
	Cone 14	1.72–11.70
Volume shrinkage, per cent	Cone 01	8.43–20.45
	Cone 4	17.85–32.40
	Cone 8	21.90–30.10
	Cone 12	3.40–41.25
Softens at cone		18–31

Stoneware clays are used not only for the manufacture of all grades of stoneware, but also for yellow ware, art ware, earthenware, and more recently even for terra-cotta.

TERRA-COTTA CLAYS

Terra-cotta is made from many different kinds of clay, but most manufacturers of this material are now using semi-fire clays, or a mixture of these with a more impure clay or shale, since these give the best results at the temperatures (cone 6–8) usually attained in their kilns. Some are used because of their dense-burning character and bonding power, others because of a low shrinkage and freedom from warping, while absence of soluble salts is an important as well as desirable property in all.

Buff-burning clays are commonly chosen, partly because they burn to a hard body at the desired temperature, and there is little danger of overburning. The color of the body is of no great importance, since the final color is applied superficially. Very few terra-cotta manufacturers at the present day employ a low-grade clay.

The soluble salts are undesirable, because in drying they may come out through the color-slip, but they can be rendered insoluble, if necessary, by treating the clay with barium chloride or carbonate.

To give a tabulated statement of the properties of clays used for terra-cotta manufacture would involve listing a very large number. It may be of interest, however, to give the properties of a terra-cotta mixture used at a large Eastern factory, the tests being made on a soft green body, as tempered at the works. Its physical properties were as follows:[1]

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[1] N. J. Geol. Surv., Fin. Rept., VI, p. 270, 1904.

Air-shrinkage, 4½ per cent; tensile strength, 97.5 lbs. per square inch. Its behavior in burning was as follows:

	Cone 01	Cone 5	Cone 10
Fire-shrinkage	1.5 per cent	4.8 per cent	5 per cent
Hardness	not steel-hard	nearly steel-hard	......
Absorption	very absorbent	slightly absorbent	nearly impervious
Color	pale buff	gray buff	gray buff

In making terra-cotta the clay is not carried to the temperature last given, as there would be danger of its warping, but it is usually fired between cones 6 and 8, at which point this danger is greatly, if not entirely, diminished.

The table on page 345 giving the physical character of some of the New Jersey clays used for terra-cotta manufacture shows what a variety of materials are employed.[1]

Wilson [2] gives the requisite property for a terra-cotta body as follows: (1) Excellent plastic working properties to permit the pressing of intricate shapes and large pieces. A minimum plastic tensile strength of 2 lbs. per square inch. (2) A maximum of 5 per cent drying shrinkage (linear). (3) Sufficient dry strength to enable the large pieces to be handled without breaking or rubbing off. The dry transverse strength should be near 350 lbs. per square inch. (4) A piece of terra-cotta approximately 1 ft. 6 in. × 1 ft. × 6 in. should dry without cracking or warping in thirty hours in the common steam drier. This can be reduced to eighteen hours in a humidity drier. Larger pieces will take a longer time. (5) The total shrinkage should not be over 1 inch per foot. (6) Good strength must be developed by cone 6. The crushing strengths of terra-cotta ware range from 3,500 to 13,500 lbs. per square inch with an average near 8,000 pounds. (7) Absorption range is from near 8.00 to 22.00 per cent. Average near 14.3 per cent. (8) The fired color must be buff, light gray or light brown.[3]

Clays suitable for terra-cotta manufacture are widely distributed, but those mostly used in this country are the Cretaceous clays of New Jersey and the Carboniferous clays of Pennsylvania, Indiana, and Missouri. Tertiary clays are also used along the Pacific Coast.

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[1] N. J. Geol. Surv., Fin. Rept., VI, 1904.

[2] Wilson, H., Bull. Amer. Ceram. Soc., V, p. 97, 1926.

[3] See Wilson, H., Monograph and Bibliography on Terra-cotta, Bull. Amer. Ceram. Soc., V, pp. 95–145, 1926.

Table showing Physical Characteristics of some New Jersey Terra-cotta Clays

Locality	Water required in tempering, per cent.	Air-shrinkage, per cent.	Tensile strength, lbs. per sq. in.	Cone of firing.	Fire-shrinkage, per cent	Color.	Hardness.
G. H. Cutter, Woodbridge.	26	4.6	57	Cone 05	4	Clay red.	Nearly steel-hard
				Cone 1	9.4	Deep red.	Nearly impervious.
				Cone 5	12	Very deep red	Impervious.
				Cone 14			Viscous.
Perth Amboy Terra-cotta Co., tendency to warp.	34	6.6	142	Cone 8	7.4	Buff.	....
				Cone 26			Vitrifies thoroughly.
Clay from Perrine's Pit, known as a stoneware clay.	37	7	109	Cone 01	6	Yellowish white.	Absorbent.
				Cone 1	6	Light buff.	Steel-hard.
				Cone 3	7.6	Buff.	....
				Cone 10	9	Gray buff.	Very dense.
				Cone 27			Incipient fusion.
J. W. Paxson & Co., Bridgeboro.	22	5.3	104	Cone 05	1.3	Pale red.	Barely steel-hard, absorbent.
				Cone 3	2.7	Light red.	Steel-hard, but absorbent.
				Cone 5	4.7	Dark red.	Absorbent.
				Cone 8	6.7	Gray.	Vitrified.
Hylton's Pits, Palmyra.	20	5.3	65	Cone 05	1.3	Buff.	Absorbent, not steel-hard.
				Cone 5	1.3	Buff.	Absorbent, not steel-hard.
				Cone 8	2	Buff.	Steel-hard, absorbent.
				Cone 27			Well vitrified.
Adams Clay Mining Co., east of Woodmansie.	23.3	5	73	Cone 5	2.7	Dirty white.	Steel-hard, absorbent.
				Cone 8	2.7	Dirty white.	Steel-hard, absorbent.
				Cone 10		Gray buff.	Small fused specks of iron silicate.

It will be seen from the above table that the clays used are mostly of low tensile strength, and that when burned at the cone number (8), at which terra-cotta is usually fired, some burned quite hard, while others were still porous. The latter kind, it will be seen, show a low shrinkage.

SEWER-PIPE CLAYS

Since the body of a sewer-pipe is vitrified or nearly so, the clays used must be such as will produce this type of body at the proper temperature. They should be sufficiently plastic to mold in the pipe press, dry and burn without warping or cracking, have good transverse strength when dry, and show freedom from soluble salts, as well as from lumpy fusible impurities. The composition should be such as will permit the taking of a salt glaze.[1] The pipe may be fired at as low a temperature as 1000° C., or usually appreciably higher.

The raw materials used may be a red burning vitrifiable shale or clay or a mixture of an impure clay with fire-clay.

In the following table there are given the analyses of sewer-pipe clays from a number of different localities.

ANALYSES OF SEWER-PIPE CLAYS

	I	II	III	IV	V
Silica (SiO_2)	57.10	55.60	63.00	59.96	57.52
Alumina (Al_2O_3)	21.29	24.34	23.57	15.76	21.76
Ferric oxide (Fe_2O_3)	7.31	6.11	1.87	7.72	3.41
Ferrous oxide (FeO)	......	......	.46	......	3.70
Lime (CaO)	.29	.43	.44	.60	.60
Magnesia (MgO)	1.53	.77	.89	.93	.88
Potash (K_2O)	3.44	3.00	2.40	3.66	3.57
Soda (Na_2O)	.61	.09	.29	......	.03
Titanium oxide (TiO_2)	......	......	1.10	......	.83
Water (H_2O)	6.00	6.75	6.45	7.70	7.27
Moisture	1.30	2.65	......	......	.86
Sulphur trioxide (SO_3)	......	......	......	.73	......
Phosphorus pentoxide (P_2O_5)	......	......	......	......	.14
Total	98.87	99.74	100.47	97.06	100.57

I. Shale, Canton, O. Ohio Geol. Surv., VII, p. 133, 1893.

II. Shale and fire-clay mixture. Ibid.

III. Underclay, Mecca, Parker County, Ind. Ind. Dept Geol. and Nat. Res., 29th Ann. Rept., p. 114, 1904.

IV. Laclede mine, St. Louis, Mo. Mo. Geol. Surv., XI, p. 570, 1896.

V. Kittanning clay. Ætna mine, New Cumberland, W. Va. W. Va. Geol. Surv., III, p. 219, 1906.

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[1] Barringer, L. E., The relation between the constitution of a clay and its ability to take a good salt glaze, Trans. Amer. Ceram. Soc., IV, p. 211. The ratio of alumina to silica should be 1 : 4.6 to 1 : 12.5.

The following figures compiled from a number of different sources will serve to show the wide range of properties exhibited by sewer-pipe clays:

RANGE OF PHYSICAL PROPERTIES OF SEWER-PIPE CLAY

Water of plasticity	per cent	18.01–36.2
Shrinkage water	per cent	10.6 –24.0
Pore water	per cent	7.6 –15.4
Linear air shrinkage	per cent	3.62–10.5
Volume air shrinkage	per cent	16.20–22.9
Modulus of rupture	pounds per square inch	190–589

Temp., ° C.	Porosity, per cent	Volume fire shrinkage, per cent	Linear fire shrinkage, per cent
990	22.59–23.50	4.73– 6.40	1.60–2.18
1090	21.38–23.45	10.32–10.36	3.57–3.58
1230	2.4 –20.1	....	3.3 –8.5
1250	10.58–12.41	15.48	5.45
1310	.4 –13.1	14.98	4.6 –9.4

The sewer-pipe clays in the Eastern and Central States are obtained chiefly from the Carboniferous formations, and to a small extent from the Devonian ones. The Cretaceous and Tertiary beds of the coastal plain States are not as a rule adapted to sewer-pipe manufacture, but in the Rocky Mountain region and Black Hills area some of the Cretaceous shales have good vitrifying qualities. Pleistocene clays are used only to mix in with the other materials. Triassic shales are used in North Carolina.

PAVING-BRICK CLAYS

The materials used for paving-brick are similar to those employed for sewer-pipe. The clays should therefore fire to a vitrified body at a relatively low temperature. They should mold easily in a stiff-mud machine, and have sufficient strength.

Shales are the most commonly used type of raw material, but low-grade fire-clays and vitrifiable plastic clays may also be employed. Carboniferous shales are extensively worked in Ohio, Pennsylvania, Indiana, and Illinois. In New York and Maryland, Devonian shales have been made use of, while in some of the Western States the Cretaceous and Tertiary shales have been found to be of importance.

The following figures give the range of composition of paving-brick clays, although little regarding their physical properties can be ascertained from them:

RANGE OF COMPOSITION OF PAVING-BRICK CLAYS *

	Minimum	Maximum	Average
Silica (SiO_2)	49.00	75.00	56.00
Alumina (Al_2O_3)	11.00	25.00	22.50
Ferric oxide (Fe_2O_3)	2.00	9.00	6.70
Lime (CaO)	.20	3.50	1.20
Magnesia (MgO)	.10	3.00	1.40
Alkalies (Na_2O,K_2O)	1.00	5.50	3.70
Ignition, loss	3 00	13 00	7.00

* Mo. Geol. Surv., XI, p. 456, 1896.

RANGE OF COMPOSITION OF IOWA PAVING-BRICK CLAYS *

	Maximum, per cent	Minimum, per cent
Silica (SiO_2)	74.58	58.56
Alumina (Al_2O_3)	22.33	8.28
Ferric oxide (Fe_2O_3)	5.75	2.88
Lime (CaO)	3.42	1.55
Magnesia (MgO)	3.47	1.22
Potash (K_2O)	1.15	.29
Soda (Na_2O)	1.79	1.08
Water (H_2O)	5.33	1.07
Carbon dioxide (CO_2)	2.23	1.73
Sulphur trioxide (SO_3)	1.85	1.28
Moisture	1.13	.28

* Ia. Geol. Surv., XIV, p. 229, 1914.

The analyses show a rather high percentage of total fluxes.

Clays for paving-brick should possess fair plasticity, since they are commonly molded by the stiff-mud process; they should have good transverse strength, and a long firing range.

The figures given below represent the range in characters of eighteen paving-brick shales and clays from Indiana, Missouri and Kansas:[1]

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[1] Purdy, Ill. Geol. Surv., Bull. 9.

PHYSICAL PROPERTIES OF SOME PAVING-BRICK SHALES AND CLAYS

	Per cent
Water plasticity	11.80–19.60
Volume air shrinkage	3.54–18.29
Linear air shrinkage	.90– 5.82
Porosity, dry,	17.80–28.86

	Pounds per square inch
Tensile strength	57–318
True specific gravity	2.41–2.73

Cones	Porosity, per cent	Specific gravity
010	26.5–28.1	2.36–2.70
08	20.8–36.4	2.48–2.7
06	25.4–33.4	2.49–2.73
04	16.2–31.6	2.44–2.72
02	15.7–26.8	2.36–2.69
1	15.5–28.0	2.41–2.68
3	6.4–22.7	2.31–2.6
5	1.4–13.4	2.05–2.47
7	1.6–12.4	1.93–2.36

BRICK-CLAYS

Common brick.—The clays or shales used for common brick are usually of a low grade, and in most cases red-burning. Calcareous cream burning ones are occasionally employed, from necessity rather than choice. The main requisites are that they shall mold easily and burn hard at as low a temperature as possible, with a minimum loss from cracking and warping. Since many common clays or shales when used alone show a higher air- and fire-shrinkage than is desirable, it is customary to decrease this by mixing some sand with the clay or by mixing a loamy or sandy clay with a more plastic one.

Common-brick clays vary widely in their composition, but most of them contain a rather high percentage of fluxing impurities.

While the chemical composition is of importance in affecting the color-burning qualities and fusibility of the mass, the physical characters are even more important, since they affect not only the color in burning, but often exert an influence on the process of molding to be chosen.

The following analyses will serve to represent their range in composition:

ANALYSES OF BRICK-CLAYS

	I	II	III	IV	V	VI	VII	VIII	IX
Silica (SiO_2)	66.67	71.50	42.28	68.62	52.30	56.50	88.71	18.62	56.81
Alumina (Al_2O_3)	18.27	13.86	8.26	14.92	18.85	19.31	4.88	3.23	20.62
Ferric oxide (Fe_2O_3)	3.11	4.78	3.84	4.16	6.55	5.89	2.00	1.26	6.13
Lime (CaO)	1.18	.56	13.05	1.48	3.36	1.00*	.30	41.30	.65
Magnesia (MgO)	1.09	.11	6.01	1.09	4.49	1.85*	.97	.42	.58
Potash (K_2O)	2.92	2.29	2.51	1.50	4.65	5.98	tr.	.....	4.47
Soda (Na_2O)	1.30	.81	.49	1.86	1.35	......	tr.	.....	.....
Titanic acid (TiO_2)	.85	1.44	.05	......	.....	......	.90	tr.	.....
Water (H_2O)	4.03	4.61	22.07	3.55	5.30	9.47†	2.28	2.42	8.60
Carbon dioxide (CO_2)	.....	.....		....	3.04	......	......	32.50	.....
Manganese dioxide (MnO_2)	.....	.....	....	.64	.....	......	......	.....	....
Moisture	.....	.....	....	2.78	.....	......	......	.....	1.64
Total	99.42	99.96	98.56	100.60	99.89	100.00	100.04	99.75	99.50

I. Pleistocene clay, Little Ferry, N. J., N. J. Geol. Surv., VI, p. 220, 1904.
II. Pleistocene clay, Richmond, Va., Va. Geol. Surv., Bull. II, p. 130, 1906.
III. Calcareous Pleistocene clay, Whitewater, Wis., Wis. Geol. and Nat. Hist. Surv., Bull. XV, 1906.
IV. Loess, Guthrie Center, Ia., Ia. Geol. Surv., XIV, p. 541, 1904.
V. Salina shale, Warners, N. Y., N. Y. State Mus., Bull. 35, p. 830, 1900.
VI. Carboniferous shale, Grand Rapids, Mich., Mich. Geol. Surv., VIII, Pt. I, p. 41, 1899.
VII. Pleistocene brick loam, Texarkana, Tex., O. H. Palm, anal.
VIII. Seguin, Guadeloupe County, Tex., O. H. Palm, anal.
IX. Residual clay, Greensboro, N. C., N. C. Geol. Surv., Bull. 13, p. 114, 1897.

* Determined as carbonate.

† Includes organic matter.

The range of characters of brick-clays, taken from a number of different sources are given below:

RANGE OF PHYSICAL PROPERTIES OF BRICK-CLAYS

	Per cent
Water of plasticity	13.2–40.70
Linear air shrinkage	0–13
	Pounds per square inch
Modulus of rupture	50–1500
Tensile strength	64–513

Temp., ° C.	Linear fire shrinkage, per cent	Porosity, per cent	Absorption, per cent
950	0– 3.4	21.8–37.8	8.62–42.58
1050	0– 9.3	....	2.73–37.20
1150	0–13.6	....	0.00–34.67
1170	0– 8.7	....	0.05–21.60

Distribution.—Common brick-clays are widely distributed both geologically and geographically. Those employed are commonly Pleistocene clays of surface character. Shales are less frequently used. Residual clays are often utilized, especially in the Southern States.

Some pretty poor clays are at times made use of for common brick manufacture, but this is due to the fact that such products will not always bear the cost of long transportation, so local sources of supply are drawn upon.

Two varieties of brick-clay, of common occurrence west of the Mississippi River, may be mentioned here.

Adobe.—This is a calcareous silty clay, common throughout the Southwestern States and much used for making sun-dried or adobe brick.

Analyses of some adobe soils, showing their calcareous character, are given below.

Loess.—This name has been applied to extensive Pleistocene deposits, which are not unlike adobe, but regarding whose origin there has been much dispute, some claiming them to be of subaqueous origin, while others consider them to be æolian formations. The loess is a very common deposit throughout the Mississippi Valley, and much used for brickmaking. Analyses by Russell[1] are given in the first table on p. 352.

Analyses of Adobe Soils

	I	II	III
Silica (SiO_2)	58.19	19.24	66.69
Alumina (Al_2O_3)	11.19	3.26	14.16
Ferric oxide (Fe_2O_3)	2.77	1.09	4.38
Lime (CaO)	12.16	38.94	2.49
Magnesia (MgO)	.80	2.75	1.28
Potash (K_2O)	tr.	tr.	1.21
Soda (Na_2O)	.18	tr.	.67
Titanium oxide (TiO_2)	1.05	......	......
Water (H_2O)	2.00	1.67	4.84
Carbon dioxide (CO_2)	8.00	29.57	.77
Phosphorus pentoxide (P_2O_5)	......	.23	.29
Sulphur trioxide (SO_3)	......	.53	.41
Chlorine (Cl)	......	.11	.34
Organic matter	......	2.96	2.00
Total	96.34	100.35	99.53

I. Laredo, Tex. O. H. Palm, analyst.
II. Salt Lake City, Utah. L. G. Elkins, analyst. U. S. Geol. Surv., Bull. 228, p. 367, 1904
III. Santa Fé, N. Mex. Ibid., p 368.

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[1] Geol. Mag., VI, pp. 289 and 342, 1889.

ANALYSES OF LOESS

	I	II	III	IV
Silica (SiO_2)	72.68	64.61	74.46	60.69
Alumina (Al_2O_3)	12.03	10.64	12.26	7.95
Ferric oxide (Fe_2O_3)	3.53	2.61	3.25	2.61
Ferrous oxide (FeO)	.96	.51	.12	.67
Lime (CaO)	1.59	5.41	1.69	8.96
Magnesia (MgO)	1.11	3.69	1.12	4.56
Potash (K_2O)	2.13	2.06	1.83	1.08
Soda (Na_2O)	1.68	1.35	1.43	1.17
Titanic oxide (TiO_2)	.72	.40	.14	.52
Phosphorus pentoxide (P_2O_5)	.23	.06	.09	.13
Manganese oxide (MnO)	.06	.05	.02	.12
Carbon dioxide (CO_2)	.39	6.31	.49	9.63
Sulphur trioxide (SO_3)	.51	.11	.06	.12
Carbon (C)	.09	.13	.12	.19
Water (H_2O)	2.50*	2.05*	2.70*	1.14*
Total	100.21	99.99	99.78	99.54

* Contains H of organic matter dried at 100° C.

Face brick.—Face brick call for a higher grade of clay. The kinds now in use fall mostly into one of three groups, namely, 1, red-burning clays; 2, white-burning clays; 3, buff-burning clays, usually semi-refractory. The composition of a sample of these three types is given in the below.

ANALYSES OF PRESSED-BRICK CLAYS

	I	II	III
Silica (SiO_2)	68.28	63.11	65.78
Alumina (Al_2O_3)	18.83	23.30	14.79
Ferric oxide (Fe_2O_3)	2.60	2.23	8.03
Lime (CaO)	.70	.73	.54
Magnesia (MgO)	.13	.97	1.42
Potash (K_2O)	2.29	.93	2.82
Soda (Na_2O)		.49	.97
Titanium oxide (TiO_2)	.27	....	1.00
Water (H_2O)	6.47	7.81	4.98
Moisture	.76	....	....
Sulphur trioxide (SO_3)	....	.24	....

I. A clay used for white brick, Grover, N. C. N. C. Geol. Surv., Bull. 13, p. 81, 1897.

II. Hocking Valley, O., clay. L. E. Barringer, analyst. Supplied by A. V. Bleininger.

III. Shale from Cayuga, Vermilion County, Ind. Ind. Dept. Geol. and Nat. Res., 29th Ann. Rept., p. 503, 1904.

The physical requirements of a pressed-brick clay are (1) uniformity of color in burning, (2) freedom from warping or splitting, (3) absence of soluble salts, and (4) sufficient hardness and low absorption when burned at a moderate temperature. The air-shrinkage and fire-shrinkage, as well as transverse strength, vary within the same limits as common bricks.

Red-burning clays were formerly much used, but in recent years other colors have found greater favor, and the demand for the former has greatly fallen off. Buff-burning, semi-refractory or refractory clays are, therefore, much employed now, partly on account of their color and partly because coloring materials can be effectively added to them, for since the range of natural colors that can be produced in burning is limited, artificial coloring agents are sometimes used. Manganese is the one most employed.

The clays must necessarily burn hard at a moderate temperature, and in the case of red-burning clays the temperature reached may range from the fusing-point of cone 06 to 2, while for buff-burning clays it is commonly necessary to go to cone 7 or 8 to get a steel-hard brick, unless calcareous materials are employed, and these are not burned above cone 3, or even cone 1.

The figures given below give the range in different properties of a number of Ohio clays used for face-brick:[1]

Physical Properties of Some New Jersey Clays Used for Face Brick *

Formation	Water required, per cent	Air-shrinkage, per cent	Average tensile strength, lbs. per sq. in	Cone of firing	Fire shrinkage, per cent	Absorption, per cent	Color
Raritan	32.00	5.0	65	Cone 1	....	....	Buff
				Cone 5	5.0	11.68	
				Cone 8	6.6	11.34	
Cohansey	23.17	7.5	282	Cone 1	2.8	8.09	Buff
				Cone 5	4.5	3.08	
				Cone 8	6.5	0.84	
Cohansey	37.50	5.5	196	Cone 8	9.1	4.01	Buff

* N. J. Geol. Surv., Fin. Rept., VI, p. 222, 1904.

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[1] Ohio Geol. Surv., 4th Ser., Bull. 26, 1923.

RANGE OF PHYSICAL PROPERTIES OF OHIO FACE-BRICK CLAYS

	Per cent
Water Plasticity	14.85–23.32
Volume air shrinkage	7.60–17.95
Linear air shrinkage	2.40– 5.66

Cone	Volume fire shrinkage, per cent	Linear fire shrinkage, per cent	Porosity, per cent
010	.97–10.51	.032–3.64	18.16–24.10
08	.40– .46	.13 – .19	22.54–23.73
03	3.27–19.88	1.10 –7.12	7.78–23.22
2	4.93–24.56	1.67 –8.97	.41–20.94
3	6.10– 8.49	2.08 –2.91	21.04–23.33
5	7.13–17.94	2.44 –6.38	6.86–17.87
7	11.48–15.99	4.16 –5.64	.06–8.25
9	11.91–14.02	4.14– 4.91	3.07– 4.00
10	8.95–15.71	3.08 –5.54	1.53– 5.40

Cone of fusion, 17–30.5.

Flashing.[1]—Many bricks used for fronts are often darkened on the edges by special treatment in firing, caused chiefly by setting them so that the surfaces to be flashed are exposed to reducing conditions, either at the end of the firing or during the entire period of burning. This color is superficial and may range from a light gold to a rich, reddish brown. The principle of the operation depends on the formation of ferrous silicate and ferrous oxide and their subsequent partial oxidation to the red or ferric form. This oxidation probably takes place during cooling, for if the kiln be closed so as to shut off the supply of oxygen, the bricks are found to be a light grayish tint.

The degree of flashing is affected (1) by the composition and physical condition of the clay, (2) the temperature of burning, (3) the degree of reduction, and (4) the rate of cooling and the amount of air then admitted to the kiln.

1. The percentage of iron oxide should not be large enough to make the brick burn red, but to produce buff coloration, and the clay should have sufficient fluxes to reduce the point of vitrification to within reasonable limits, thus facilitating the flashing. Clays high in silica are apparently better adapted to flashing than those low in silica and high in alumina. The condition in which the iron is present in the clay probably

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[1] A. V. Bleininger, Notes on Flashing. Trans. Amer. Ceramic Soc., II. p. 74.

exerts some influence, that is, whether it is there as ferric oxide, ferrous silicate, concretionary iron, ferrous sulphide, or perhaps ferrous carbonate. Bleininger's experiments showed that of three clays which were used for flashing, all contained considerable quantities of iron soluble in acid. Some Eastern manufacturers are obliged to add magnetite ores to their clays, which are low in combined iron, and No. 2 fire-clays, which contain more iron than the finer grades, seem to give the best results. As to the effect of the physical condition of the clay, finer grinding seems to give more uniform flashing effects, and the reason that stiff-mud bricks flash better than dry-press ones is claimed by some to be due to vitrification taking place more easily in the former.

The following analysis gives the composition of a No. 2 fire-clay from Ohio used for flashed brick:

ANALYSIS OF AN OHIO NO. 2 FIRE-CLAY

Silica (SiO_2)	67.14
Alumina (Al_2O_3)	19.74
Ferric oxide (Fe_2O_3)	2.46
Lime (CaO)	0.53
Magnesia (MgO)	0.71
Potash (K_2O)	2.80
Soda (Na_2O)	0.43
Water (H_2O)	7.01
Total	100.82

In one case the green clay showed a total of 2.15 per cent of ferric oxide, of which 0.88 per cent was soluble in acid. The flashed surface of a brick made from this clay gave, on analysis, a total of 2.31 per cent of ferric oxide, of which 0.14 per cent was soluble in nitro-hydrochloric acid, thus indicating that during the burning most of the iron oxide had combined with silica, forming a ferrous silicate.

2. The temperature reached must be sufficient to cause a combination of the iron and silica, and, therefore, it varies with different clays, the combination being aided by the presence of fluxes.

If the kiln atmosphere is oxidizing during nearly the entire burning, with only a small period of reduction at the end, the temperature reached must be comparatively high in order to insure union of the iron and silica by fusion. If, however, a reducing fire is maintained during most of the burning, then the temperature need not be as high, because the clay will vitrify sooner. (See Fusibility, Chapter V.)

At one factory it had formerly been the practice to burn with an oxidizing fire to a high temperature, namely, from cone 11–12, and then to cause reducing conditions to take place in the kiln during the last five or six hours of the burn. This practice, however, was changed, it being found that by maintaining a reducing fire during the entire period following water smoking a lower temperature was sufficient.

3. The oxidation which causes the flashing probably takes place in the first twelve hours after closing the kiln, and can be regulated by a proper handling of the dampers.

In the experiments of Bleininger, already referred to, it was found that a reduction of air, equal to 20 per cent below that required for ideal oxidation and considered as 100, is usually sufficient to produce flashing.

By this is meant that "100 per cent of air represents theoretically ideal conditions, in which just enough air is present to consume all the combustible gases forming CO_2; less than 100 per cent of air corresponds to reducing conditions. For instance, if an analysis on calculation represents 90 per cent of air, it tells us that the gases are reducing to the extent of 10 per cent of air; similarly, 110 per cent shows an excess of air to the amount of 10 per cent."

While 100 per cent represents theoretically the amount of air required for perfect combustion, still in actual practice with coal-fuel the mixture of gases is not perfect, and it may be necessary to have more than 100 per cent of air present to bring about thorough oxidation.

4. As regards the rate of cooling, it was found that the longer the period of cooling from the maximum temperature down to approximately 700° C. the darker the flash under given conditions.

Enameled brick.—The clays used for these are similar to those employed in the manufacture of buff pressed brick. The enamel is, of course, an artificial mixture, but must conform to the clay body to avoid cracking or scaling off of the coat.

FIREPROOFING AND HOLLOW-BRICK CLAYS

The clays used for making hollow bricks and fireproofing vary with the locality. At not a few yards where red bricks are manufactured the red-burning surface-clays of Pleistocene age are employed. In New Jersey, where many thousand tons are annually produced to supply the New York and other large Eastern markets, a mixture of red-burning sandy clay and a small amount of low-grade fire-clay are chosen, while in the States of the Eastern and Central coal-measure areas, as in Pennsylvania, Ohio, Indiana, and Illinois, Carboniferous shales are widely used.

It is therefore difficult to lay down any fixed set of requirements for the raw materials of this class. This much can be said: They should have sufficient plasticity to flow smoothly through the peculiar shape of die used in making them; they should also possess fair tensile strength; burn to a good hard but not vitrified body at a comparatively low cone. Concretionary masses, if present, should be either removed or crushed.

The following analyses show well the composition of clays or shales used for this kind of ware:

ANALYSES OF CLAYS USED FOR HOLLOW BRICK AND FIREPROOFING

	I	II	III
Silica (SiO_2)	52.22	57.57	51.95
Alumina (Al_2O_3)	29.43	21.70	18.34
Ferric oxide (Fe_2O_3)	2.78	2.26	7.56
Ferrous oxide (FeO)	....	4.11	....
Lime (CaO)	.88	.32	4.14
Magnesia (MgO)	.72	1.12	3.36
Potash (K_2O)	2.10	2.16	1.43
Soda (Na_2O)	.75	.33	2.69
Titanium oxide (TiO_2)	....	1.10	....
Water (H_2O)	11.10	6.78	7.39
Moisture		.....	.42
Carbon dioxide (CO_2)	....	1.73	....
Sulphur trioxide (SO_3)	....	....	2.76

I. National Fireproofing Co., Keasbey, N. J. N. J. Geol. Surv., Final Report, VI, p. 282, 1904.
II. Underclay beneath Coal II, Cannelton, Ind. Ind. Dept. Geol. and Nat. Res., 29th Ann. Rept., p. 338, 1904.
III. Representative shale-clay from Iowa. Ia. Geol. Surv., XIV, p. 232, 1904.

The physical tests of fireproofing clays shown on p. 358 are given in the New Jersey Geological Survey report.[1]

The tabulation is not without interest, and shows a considerable variation in certain directions. The air-shrinkage shows little variation, but the tensile strength shows a great range. Of these different samples, Nos. 1, 2, and 6 are practically from the same bed. No. 5 is from the base of the Raritan series, and is one of the most dense-burning clays to be found in that section or even New Jersey. Most of these clays have to be burned to cone 01 before becoming steel-hard, the one exception being No. 5, which burns very hard at cone 05. They all burn red. The pyrite and limonite nodules are abundant in some of the layers, and in burning often fuse, swell, and spall off pieces of the ware.

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[1] Ia. Geol. Surv., XIV, p. 229, 1904.

TESTS OF NEW JERSEY CLAYS USED FOR FIREPROOFING

Locality.	Water required to temper, per cent.	Air-shrinkage, per cent.	Average tensile strength.	Cone of firing.	Fire-shrinkage, percent.	Color.	Hardness
1. Perth Amboy, black clay, small lumps of pyrite and lignite.		5	145	Cone 05.	1.6	Gray red.	Not hard.
				Cone 01.	2	Red.	Hard.
				Cone 3.	2.9	Red.	Hard.
				Cone 15 to 16.			Viscous at 1440° C.
2. Perth Amboy district, similar to the preceding.		5.5	112	Cone 05.	2.5	Reddish.	Not hard.
				Cone 01.	3	Red.	Hard.
3. Lorillard.		6	238	Cone 05.	2.6	Red.	Fairly hard.
				Cone 01.	4	Red.	Hard.
				Cone 1.	5		
				Cone 13 to 14.			Viscous at 1400° C.
4. Spa Spring, gritty clay, moderate plasticity.		5.5	50	Cone 05.	2.5	Red.	Not hard.
				Cone 1.	2.5	Red.	Hard.
				Cone 3.	3.4	Red.	Hard.
				Cone 10.	11.5	Speckled gray brown.	Nearly vitrified.
5. Piscataway red clay, quite plastic.	36	7	129	Cone 05.	4	Deep red.	Hard.
				Cone 01.	10	Red.	Vitrified.
				Cone 3.	10.7	Deep red.	Well vitrified.
6. South River, dark-gray clay, mica scales and organic matter.	25	.	84	Cone 1.	8	Red.	Hard.
				Cone 5.	10.7		Vitrified.
7. Shale from Port Murray.	18.5	2	51	Cone 05.	1.6	Pale red.	Easily scratched.
				Cone 01.	2.4	Deep pink.	Scratched.
				Cone 1.	4.6	Red.	Scratched.

Roofing-tile Clays[1]

The clays required for roofing tile should possess good plasticity and strength when dry, and because of the flat shape of the product it is essential that the material should show freedom from warping and cracking in the drying and burning. Ease of oxidation, wide vitrification range, and proper color after firing are also important. The clays or shales employed are commonly red burning, but other types have been used. If the tile is unglazed it should be fired to a hard, dense body, but if a glaze is applied, vitrification is not as complete.

Slip-clays

A slip-clay is one containing such a high percentage of fluxing impurities, and of such texture that at a low cone it melts to a greenish or brown glass, thus forming a natural glaze. It must be fine grained, free from lumps or concretions, show a low air-shrinkage, and mature in burning at as little above cone 5 as possible.

While easily fusible clays are not uncommon, all do not melt to a good glaze.

" A good slip-clay makes a glaze which is free from defects common to artificial glazes. It will fit a wide range of clays, and since it is a natural clay it will undergo the same changes in burning as the body on which it is placed. Artificial mixtures of exactly similar composition to the natural clays have failed to give the excellent results as to gloss or color that are attained by the natural clay."[2]

While several fair slip-clays have been found in different parts of the country, none have given thorough satisfaction except the Albany, N. Y., material, which is shipped to all parts of the United States for potters' use.

In applying the glaze to the ware the clay is mixed with water to a creamy consistency and applied to the ware either by dipping or spraying. Attempts have sometimes been made to lower the fusing-point of the slip by the addition of fluxing oxides.

The following are analyses of slip-clays:

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[1] For a detailed report on roofing tile manufacture see Worcester, Ohio Geol. Surv., 4th Ser., Bull. 11, 1910.

[2] N. J. Geol. Surv., Fin. Rept., VI, p. 280, 1904.

ANALYSES OF SLIP-CLAYS

	I	II	III	IV	V
Silica (SiO_2)	55.60	43.94	63.63	38.08	57.01
Alumina (Al_2O_3)	14.80	11.17	13.57	11.36	11.85
Ferric oxide (Fe_2O_3)	5.80	3.81	7.77	2.60	3.02
Lime (CaO)	5.70	11.64	2.55	23.70	9.56
Magnesia (MgO)	2.48	4.17	1.47	tr.	1.20
Potash (K_2O)	3.23	2.90	2.63	.58	.75
Soda (Na_2O)	1.07	.71	.88	1.60	2.01
Manganese oxide (MnO)	.14	......	......	......	......
Titanium oxide (TiO_2)	......	......	......	.70	1.13
Phosphorus pentoxide (P_2O_5)	.15	......	......	......	......
Water (H_2O)	5.18	3.90	4.75	3.06	4.00
Carbon dioxide (CO_2) and moisture	4.94	15.66	2.90	18.80	8.00
Total	99.09	97.90	100.15	100.48	98.53

I. Albany, N. Y. Ohio Geol. Surv., VII, p. 105, 1893.
II. Rowley, Mich. Ibid., p. 105.
III. Brimfield, O. Ibid., p. 105.
IV. Leon Creek near San Antonio, Tex. O. H. Palm, analyst.
V. Alazan Creek near San Antonio, Tex. O. H. Palm, analyst.

The use of slip-clays for glazing stoneware is decreasing each year, because an artificial white glaze is now usually preferred.

Gumbo-clay.—Under this name there are included certain fine-grained, highly plastic, tenacious clays of surface character, which are found at many points in the Western Central States. Their high shrinkage and dense character prohibits their use for brickmaking, but they are found excellently adapted to the manufacture of railroad ballast.

Wheeler, in describing the Missouri occurrences,[1] states that they do not differ chemically from common brick, paving brick, sewer-pipe or other burnt clays, and "their peculiar value for burnt ballast is entirely a physical one." He gives the following variation in composition:

Silica (SiO_2)	55 –65
Alumina (Al_2O_3)	15 –20
Ferric oxide (Fe_2O_3)	5 – 7
Lime (CaO)	1 – 3
Magnesia (MgO)	.5 – 2
Alkalies (Na_2O, K_2O)	2.5 – 4
Water (H_2O)	6 –10
Fluxes	10 –15

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[1] Mo. Geol. Surv. XI, p 543, 1897.

Their physical properties range as below:

Water required	22–25 per cent
Average tensile strength	270–410 lbs. per sq. in.
Air shrinkage	8–10 per cent
Fire shrinkage	1–6 per cent
Incipient vitrification	1600°–1700° F.
Complete vitrification	1750°–1850° F.
Viscosity	1900°–2000° F.

Retort-clay.—A dense-burning, plastic, semi-refractory clay used chiefly in the manufacture of gas-retorts and zinc-retorts. In New Jersey the term is often applied to stoneware-clays.

Ware-clay.—A term sometimes used for ball-clays, especially in the Woodbridge, N. J., district.

Pipe-clay.—This is a term applied to almost any fine-grained plastic clay. Strictly speaking, it would refer to a clay used for making sewer-pipe.

Wad-clay.—This is a low grade of fire-clay, which is used for grouting the joints between the saggers when they are set up in bungs in the kilns.

Portland-cement clay.—The use of clay or shale for Portland cement is the most important of what may be termed the minor uses of clay. Portland cement is essentially an artificial mixture of lime, silica, and alumina. The first of these is usually supplied by some form of calcareous material, such as limestone, marl, or chalk, while the other two are obtained by the selection of clay or shale, the mixture consisting approximately of 75 per cent lime carbonate and 25 per cent clay or shale.

Clays or shales to be used for Portland-cement manufacture should be as free as possible from coarse particles or lumps of sand, gravel, or concretions. These conditions are best met by the transported clays, since residual clays are frequently sandy or stony, and many glacial clays notably so. An examination of the analyses of clays used at different works in this country shows that the silica percentage ranges from 50 to 70 per cent; when calcareous clays are used it may fall below 50 per cent.

The analyses shown on p. 362 give the composition of clays employed at a number of different localities.

It is not to be understood from what has been said above that the clays whose analyses are given can be used only for Portland-cement manufacture; indeed nearly all of them could be utilized for some kind of clay product.

Analyses of Portland-cement Clays

	I	II	III	IV	V	VI
Silica (SiO_2)	53.30	63.73	74.29	64.85	55.27	40.56
Alumina (Al_2O_3)	23.29	22.12	12.06	17.98	10.20	8.52
Ferric oxide (Fe_2O_3)	9.52	9.01	4.92	5.92	3.40	2.84
Lime (CaO)	.36	2.83	.41	2.24	9.12	20.94
Magnesia (MgO)	1.49	....	.68	1.40	5.73	1.32
Potash (K_2O)	1.36	.21	.76	....	....	1.97
Soda (Na_2O)	2.76		1.80	....	....	
Sulphur trioxide (SO_3)	....	....	....	....	....	....
Carbon dioxide (CO_2)	....	....	....	4.98	......	17.90
Water (H_2O)	5.16	....	....		......	5.95

	VII	VIII	IX	X	XI
Silica (SiO_2)	57.98	61.09	54.30	61.92	55.27
Alumina (Al_2O_3)	18.26	19.19	19.33	16.58	28.15
Ferric oxide (Fe_2O_3)	4.57	6.78	5.57	7.84	
Lime (CaO)	1.75	2.51	3.29	2.01	5.84
Magnesia (MgO)	1.83	.65	2.57	1.58	2.25
Potash (K_2O)	....	1.8	....	3.64	
Soda (Na_2O)	....	1.36	....		
Sulphur trioxide (SO_3)	1.28	1.42	2.36	tr.	.12
Carbon dioxide (CO_2)	12.08	5.13			
Water (H_2O)			....	....	....

I. Little Rock, Ark. Amer. Inst. Min. Eng., Trans., XXVII, 62.
II. Santa Cruz, Cal. Min. Indus., I. p. 52.
III. Bedford, Ind. Ind. Dept. Geol. and Nat. Res., 25th Ann. Rept., p. 328.
IV. Millbury, O. Mich. Geol. Surv., VIII, Pt. III, p. 229.
V. Syracuse, Ind. Ind. Dept. Geol. and Nat. Res., 25th Ann. Rept., p. 28.
VI. Bristol, Ind. U. S. Geol. Surv., 21st Ann. Rept., Pt. 6 (ctd.), p. 400.
VII. Yankton, S. Dak. Min. Indus., VI, p. 97.
VIII. Alpena, Mich. Mich. Geol. Surv., VIII, Pt. III, p. 227.
IX. La Salle, Ill. U. S. Geol. Surv., 20th Ann. Rept., Pt. 6 (ctd.), p. 544.
X. Catskill, N. Y. Supplied by company.
XI. Glens Falls, N. Y. Min. Indus., VI, p. 97.

Clays Used in Unburned Condition

Polishing and abrasive materials.—Many clays exert a combined polishing and abrasive action, on account of the very finely divided grains of sand which they contain. The well-known Bath brick which has such an extensive domestic use for scouring steel utensils is simply a fine-grained siliceous clay, which is deposited during high tide along the banks of the Parrot River in England.

Some clay is used for bonding purposes in the manufacture of abrasive wheels. These are burned before use, so that the clay vitrifies and holds the abrasive grains together.

FILLER CLAYS[1]

Under this head are included those clays which are used chiefly as a filler in the manufacture of such materials as paper, paint, rubber, etc. They are chiefly white clays of sedimentary or residual character, although some off-color ones are employed, and they commonly require refinement by washing or some other method before shipment to market.

There are no universely accepted standard requirements or tests, although the different manufacturers have certain ones which they may apply.

Paper clays.—Clays may be used for coating or filling paper. Most of the coating clays now used are imported, but domestic ones are extensively employed as a filler.

The important physical properties are freedom from grit, color and retention.

The clay must be free from grit, as this cuts the wires of the screens and scratches the surface of the calendar rolls. The use of a screen test is suggested using a 325-mesh screen, on which good clays leave 1 per cent or less residue.

Color is very important for high-grade papers, which call for a white clay. A rough comparison of color can be made by placing several samples side by side, but this cannot be expressed numerically. A Pfund colorimeter was used by Weigel, which permitted comparisons expressed numerically. For inferior papers color may be of less importance.

Retention refers to the quantity of clay retained by the fibers of the paper and varies with different clays.

Rubber clay.—Clay is used in some quantity in rubber manufacture. The only reliable way to determine its value appears to consist of actually compounding this with the other ingredients used in rubber, and then subjecting the compound to standard physical tests.

In the tests listed by Weigel these mixtures were cured at 300° F., for 20, 30, 40, 60 and 90 minutes. After aging twenty-four hours, the test-pieces were broken in a Scott testing-machine, and their tensile strength in pounds per square inch given. The hardness was determined by a Shore durometer, and the ultimate elongation also measured.

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[1] The writer has drawn freely on a report by W. M. Weigel, U. S. Bur. Mines, Tech. Pap. 343, 1925. See also: Gwynne, C. S., Trans. Amer. Ceram. Soc., XIV, p. 571, 1912; Roe, R. B., Jour. Amer. Ceram. Soc., II, p. 69, 1919; Shaw, M. B., and Bicking, G. W., U. S. Bur. Stand., Tech. Pap. 262, 1924.

Oilcloth.—The testing methods for determining the value of clay in oilcloth manufacture are not standardized. In general Weigel says a clay for oilcloth should be white, free from grit, should slake readily to a smooth cream or slip without lumps, and have a comparatively low oil absorption. It is claimed by some that English clays take less oil than American ones.

Paint.—Manufactures of paint demand in general a white gritless plastic clay, which is used to mix with the colors. In general the material is similar to that demanded by the paper makers, although the requirements as to minute differences in shades of color and grit would seem not to be quite as severe, although one manufacturer stated the clay should pass a 300-mesh sieve. Irregularity in product, as in other uses, is seriously objected to.[1]

Certain ferruginous clays and also shales, when ground and mixed with oil, make a good grade of mineral paint. Their color in most cases is due to some form of iron oxide, or more rarely manganese. Ocher is often nothing more than a fine-grained furruginous clay colored by limonite, and the same may be true of sienna.

Mineral paints made from clays and shales form a cheap and satisfactory form of pigment for application to wooden surfaces. The value of the material depends to a large extent on the shade of color, its texture, and the amount of oil that has to be mixed with it in order to get the proper degree of fluidity.

Ultramarine manufacture.—Washed kaolin or even very fine-grained white sedimentary clays are used in the manufacture of ultramarine to serve as a nucleus for gathering the coloring material. For this work the clay should be as low in iron or lime as possible, and an excess of silica is undesirable.[2]

Miscellaneous uses of filler clays.—Coating wall paper, in plaster and plaster products, filling for textiles and window shades, kalsomine, crayons, toilet and tooth powders, soaps, soft polishing compounds, phonograph records, and matches, include various minor uses of filler clays. In all of these whiteness and freedom from grit are the qualities most desired.

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[1] See also: Gardner, H. A., Paint technology and tests, N. Y., 1911; Ingalls, F. P., Uses of silica and other mineral fillers in paint, Rock Products, Feb. 26, 1921, to May 7, 1921; Chem. Age (London), China Clay in paints, China Clay Rev. Sec., July 21, 1923, p. 11.

[2] See also Sauvegeot, Rev. prod. chim., Apr., 1921, and Tonind.-Zeit., XLV, p. 494, 1921; Dominikiewicz, M., Roozniki Chem., V, p. 308, 1925, and Chem. Abs., XX, 1578.

Sources of supply.—While English clay has been extensively used as a filler in both the United States and Canada, the white sedimentary clays of South Carolina and Georgia are being used more and more for this purpose.

Consumption.—Weigel gives the following figures to show the amount of domestic clays sold for filler in one year:

Use	Short tons
Paper filler	102,732
Paper coating	9,031
Rubber	15,279
Oilcloth and linoleum	8,165
Paint filler or extender	13,328
Paint pigment	259
Plaster and plaster products	5,582
Kalsomine	2,386
Crayons	1,009
	157,771

BENTONITE

Definition.—This is a widely distributed and peculiar type of clay which is considered to be the result of devitrification and chemical alteration of the glassy particles of volcanic ash or tuff.

The material was originally called *Taylorite* after William Taylor of Rock Creek, Wyoming, who first called attention to it, but as this name had already been allotted to another mineral the name of *Bentonite* was used, because of its occurrence in the Fort Benton series of rocks.

Microscopic characters.—The study of thin sections shows that bentonite is derived from volcanic ash,[1] and that its characteristic mineral, *montmorillonite,* is definitely crystalline. Many sections show the ash structure, while glass fragments of various and characteristic shapes are present.

According to Ross and Shannon (Ref. 7) it " often contains variable proportions of accessory crystal grains that were originally phenocrysts in the volcanic glass. These are feldspar (commonly, orthoclase and (oligoclase), biotite, quartz, pyroxenes, zircon, and various other minerals typical of volcanic rocks."

[1] Hewett, D. F., Jour. Wash. Acad. Sci., VII, p. 196, 1917; Wherry, E. T., *ibid.,* VII, p. 576, 1917.

"The characteristic clay-like mineral has a micaceous habit and easy cleavage, high birefringence and a texture inherited from volcanic tuff or ash, and it is usually the mineral montmorillonite, but less often beidellite."

Single glass fragments may be made up of a series of parallel plates. These plates usually stand perpendicular to the original surface of the glass fragment, but at times they may have developed parallel to the sides of the glass. The high birefringence shows only when the micaceous plates stand perpendicular to the thin section and plates that lie nearly parallel are black or dark gray (Ref. 7, p. 83).

Bentonite does not contain an abundance of amorphous gel material, but it does carry a large amount of finely divided crystalline substance, and in this sense is colloidal. Its high adsorptive powers are due to its physical structure.

It is suggested that the name bentonite be restricted to material derived from volcanic ash. As also pointed out by Ross and Shannon, bentonite may contain foreign detrital material from different sources in addition to the igneous rock phenocrysts, while varying amounts of admixed sands may be present.

The appearance of bentonite varies greatly. Pale buff, cream or dull cream are probably common colors, but gray, dull blue, greens, pinks, red and yellow are also seen.

The texture is often compact, with a conchoidal fracture, but other specimens are open and porous.

Small grains of calcium or iron carbonate may be present, and manganese oxide spots, gypsum and barite crystals have been noted in others.

Origin.—It is not always possible to state definitely what the original composition of the bentonite was (Ref. 7). Feldspar (usually orthoclase) is the predominant phenocryst, but biotite is not rare. The phenocrysts are usually those characteristic of quartz-free trachytes, latites, quartz latites, and possibly quartz poor rhyolites, but rarely quartz-rich rhyolites. An arkosic bentonite has been derived from nephelite-bearing rocks, while an iron-rich one is derived from olivine basalt. The suggestion has been made that glasses very high in silica are rather stable and consequently do not alter readily to bentonite. Those with an intermediate silica content approaching a feldspar glass in composition alter to montmorillonite with a 1 : 5 alumina-silica ratio, and those low in silica to beidellite with a 1 : 3 ratio.

The conditions favoring the alteration of glass to bentonite are not well known. We cannot definitely ascribe it to the action of salt water because all bentonites are not found in marine sediments, unless we assume that the ash may have fallen into saline lakes. The alteration process involves hydration, devitrification, and leaching of alkalies as well as other bases. The wide distribution of bentonite also suggests that the alteration is not due to any special condition.

Some have suggested that volcanic gases played a role in at least starting the alteration.

The fact that some bentonites contain much non-volcanic detrital material also suggests that the ash may have been deposited on land, and later carried by erosion into bodies of water.

The clay mineral montmorillonite is the chief one in most bentonites, but in a few beidellite is the dominant one. Both of these minerals have been found in other types of deposits.

Ross and Shannon state: " These minerals have different chemical compositions but resemble each other in being obviously crystalline and often rather coarsely crystalline, in possessing a platy, or micaceous habit and easy cleavage, and rather high birefringence. They resemble the micas in many ways and may sometimes be mistaken for them, and they differ in many ways from kaolinite and halloysite. Beidellite and the micaceous mineral corresponding to halloysite have somewhat higher indices of refraction and higher birefringence than montmorillonite, but all are characterized by a high water content. Beidellite and montmorillonite have heretofore been grouped with leverrierite and the other mineral has not been differentiated from halloysite."

Physical properties.—The physical properties of bentonites vary. The majority swell slightly and crumble in water, but develop no plasticity. Some show strong swelling,[1] develop plasticity, and contain a large amount of material that remains in permanent suspension. The difference is assigned in part to variations in structure, and in part to natural salts that act as flocculating and deflocculating agents. The swelling is thought to be due to films of water forming between the plate-like grains.

Colloids.—Wherry [2] has suggested the term " one dimensional " colloid for the very thin micaceous plates of dispersed bentonite. These he states " exhibit optical and physical properties which indicate that their grains are of visible dimensions in two-space directions but submicroscopic and colloidal in the third, perpendicular to the mica-like plates." This gives the material great surface area and high adsorptive powers.

In the case of some bentonites which at first yield only slight suspensions, prolonged agitation may greatly increase the amount of dispersed material, which Spence (Ref. 10) thinks is due to increased hydration.

[1] Spence mentions one that swelled 13.8 times in volume (Ref. 10).

[2] Jour. Mineral. Soc. Amer., X, p. 65, 1925.

Chemical composition.—The analyses on pp. 368 and 369 represent crude material:

Analyses of Crude Bentonite from United States

	I	II	III	IV	V	VI
SiO_2	51.10	50.30	49.56	51.56	50.33	54.00
TiO_2	....	....	.40	.78	....	....
Al_2O_3	15.40	15.96	15.08	13.42	16.42	24.48
Fe_2O_3	4.50	.86	3.44	3.22	2.42	3.00
MnO	....	....	.01	....	....	....
CaO	5.20	1.24	1.08	2.04	1.39	2.08
MgO	3.80	6.53	7.84	4.94	4.10	2.75
K_2O	1.50	.45	....	.38	1.00	....
Na_2O		1.19	....	.24	.12	1.74
P_2O_5	....	....	....	....	....	0.71
H_2O	17.10	23.61	22.96	23.46	23.95	9.12
Total	98.60	100.14	100.37	100.04	99.73	97.88

I. Selected crude, Ardmore, S. Dak., E. T. Wherry, analyst.
II. Bentonite (otaylite) crude selected white material, near Otay, San Diego Co., Calif., J. E. Whitfield, analyst.
III. Otaylite, crude selected pink, near Otay, San Diego Co., Calif., E. V. Shannon, analyst.
IV. Pink friable matrix of bentonite tuff. Three miles north of the east end of Tierra Amarilla grant, New Mex. Purified.
V. Selected crude bentonite, Maricopa, Kern Co., Calif., E. V. Shannon, analyst.
VI. Supposed bentonite, near Shelbyville, Tenn.

Nos. I to IV from Ross and Shannon, Ref. 7.

Spence states that alkaline salts, notably sodium sulphate, are often found near bentonite deposits, and that a scum of such salts is often noticed around the out-crops. Gypsum is likewise conspicuous around some. The clay, too, usually contains appreciable amounts of Na_2O. The latter is strongly adsorbed in the clay. The most highly colloidal bentonites are found on analysis to contain the highest percentage of soda.

Effect of electrolytes.—Spence suggested that the electrolytes which might be present in bentonite are sodium sulphate, alum or even weak sulphuric acid, products of mineral decomposition.

He gives the results of a number of tests to determine the flocculating effect of various reagents upon bentonite-water suspensions. These tests show that, as is known, that the valence of the metal ion is a measure of the flocculating power of the electrolytes, those of higher valence being most active. It appears that the hydrogen ion is a flocculator, while the hydroxyl ion is a deflocculator.

ANALYSES OF CRUDE BENTONITES FROM CANADA

	I	II	III	IV	V
SiO_2	69.70	68.60	54.88	59.80	60.78
Al_2O_3	14.00	12.10	19.92	16.36	17.08
Fe_2O_3	2.88	2.00	4.10	2.23	3.67
FeO	0.23	0.32	0.22	3.52	0.43
CaO	1.56	1.84	2.22	1.82	2.84
MgO	1.81	1.84	2.83	2.67	2.16
TiO_2	0.23	0.14	0.25	0.05	0.22
P_2O_5	0.01	0.17	0.09	tr.	0.03
Na_2O	1.09	0.50	1.75	2.00	1.54
K_2O	0.29	0.23	0.26	0.27	0.46
S	0.02	0.00	0.00	0.00	0.04
H_2SO_4	0.00	0.61	0.16	0.00	0.01
CO_2	0.04	0.17	0.37	0.72	1.11
C	0.09	0.08	0.07	0.09	0.13
H_2O.105° C.	3.92	7.71	8.10	5.18	5.94
$H_2O+105°$ C.	4.28	3.24	4.28	4.91	3.70
Total	100.15	99.55	99.50	99.62	100.14

I. Quilchena, near Merritt, Brit. Col.
II. Princeton, Brit. Col.
III. Rosedale, Alberta. Surface outcrop.
IV. Rosedale, Alberta. From coal mine.
V. Camrose, Alberta.

Nos. I to V from Spence, Ref. 10.

Physical tests.—The following physical properties of certain bentonites are given by Spence:

	I	II	III	IV
Quilchena, B. C.	1.53	2.44	1430° C.	1.547
Camrose, Alta	4.15	2.73	....	....
Rosedale, Alta	4.71	2.72	1410° C.	1.568
Newcastle, Wyo	4.93	2.77	1350° C.	1.557
Medicine Bow, Wyo	4.95	2.78	1330° C.	....

I. Water in grams absorbed by 1 gm. bentonite.
II. True sp. gr.
III. Fusion point.
IV. Refractive index.

Settling tests.—Ten grams of crude bentonite were placed in 350 c.c. water and agitated for three hours. It was then screened through a

200-mesh screen, the oversize washed with 150 c.c. water, dried and weighed.

The mixture passing screen was allowed to stand twenty-four hours and then decanted. The settled clay was also dried and weighed.

Settling Tests of Bentonite

	I	II	III
Quilchena, B. C.	2.18%	76.72%	21.10%
Rosedale, Alta.	1.58	10.10	88.32
Camrose, Alta.	3.16	13.14	83.70
Newcastle, Wyo.	0.95	29.75	69.30
Medicine Bow, Wyo.	1.21	11.59	87.20

I. 200-mesh.
II. Settled clay.
III. Dispersed clay.

Effect of heating.—Spence states that heating produces a marked decline in the colloidal and distention properties of bentonite. Moisture determinations were made on several bentonite samples after heating to temperatures given below, but at even the highest temperature some water of combination still remained although the colloidal behavior was destroyed.

Effect of Heating on Bentonites

	Moisture content of air dry clay, Per cent	Water content after heating to				
		450° C., Per cent	500° C., Per cent	550° C., Per cent	600° C., Per cent	700° C., Per cent
Quilchena, B. C.	4.64	4.04*	3.94	....	2.53	1.50
Camrose, Alta.	3.70	....	3.60*	....	2.09	1.14
Rosedale, Alta.	4.28	....	....	4.17*	....	....
Newcastle, Wyo.	3.67	....	3.49	....	3.43*	0.77

* Swelling property completely destroyed.

Dilution of bentonite-water suspension.—The effect of the degree of dilution, and time, on a bentonite-water suspension was tried by taking four 10-gram samples of Rosedale bentonite and completely disintegrating by agitation in 350 c.c. water. These solutions were made up to

500, 1000, 1500 and 2000 c.c., respectively, and the amount still in suspension determined after 1, 4, 6, and 10 days as below:

	Clay in suspension after			
	1 day, Per cent	4 days, Per cent	6 days, Per cent	10 days, Per cent
500 cc. dilution....	88.46	87.25	87.25	60.72
1000 cc. dilution....	86.52	74.05	63.40	56.70
1500 cc. dilution....	85.41	71.25	58.30	48.50
2000 cc. dilution....	83.26	60.11	55.00	42.60

With still greater dilution up to 5 litres and four months' standing it was found that the suspended material decreased with increased dilution.

These figures indicate that time and degree of dilution have an important influence, and that in conducting comparative dispersion tests a constant time factor and degree of dilution should be employed to get comparable results. The effect of temperature was not determined.

Occurrence.—Bentonite always occurs in bedded deposits ranging from a few inches to as much as 10 feet in thickness.

It is found interstratified with sands, clays or shales, and in some of the sections published from Western Canada, it is seen to immediately overlie or underlie beds of lignite at certain localities. One section in the Cretaceous deposits near St. Victor, Saskatchewan, shows a deposit of gray volcanic ash with layers of ironstone nodules grading upward into bentonite.

The outcrops of bentonite show a rather characteristic weathered surface, with a crinkled, coral-like appearance, caused by alternate swelling and shrinking due to repeated wetting and drying.

Distribution of Bentonite.—Bentonite is a most widely distributed material having been reported from every State west of the Missouri River, as well as from Kansas, Oklahoma, Texas, Louisiana, Arkansas, Tennessee, Alabama, Virginia, Kentucky, Pennsylvania, Minnesota, Wisconsin, etc. In Canada bentonite deposits have been noted in Manitoba, Saskatchewan, Alberta and British Columbia. It has also been found in Alaska and foreign countries.

Its known geological range is from the Ordovician to Tertiary.

Uses.—Bentonite may be found to be useful for a number of purposes, but the demand for it at present is limited.

One possible trouble may be the difficulty of cleaning the material in order to rid it of sand, gypsum and carbonaceous matter.

Among the possible uses listed by Spence are: As an adsorbent; as a retarding agent in gypsum plasters; as a suspending agent in pottery glazes; for dewatering petroleum, gasolene and different oils; in the dye industry as a mordant and as a base for lake colors; as an accelerator and stabilizer in emulsions made up of water and various oils, fats and resins; for fertilizer filler; in foundry work as a bond for sand; as a sticking or spreading agent in insecticidal sprays and dusts; as a filler in paints; as a substitute for clay in pencils and crayons; for pharmaceutical uses and in cosmetics; in soaps; and as a water-softening agent.

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FULLERS' EARTH

PROPERTIES

Fullers' earth is a peculiar type of clay which has a high absorbent power for many substances, on which account it is used for decolorizing oils and other liquids. The statement usually seen in print that it lacks plasticity and falls to pieces in water is misleading and of no value. When dried, fullers' earth often adheres strongly to the tongue, but so do some ordinary clays which have no clarifying powers. The color is also variable. Its specific gravity ranges from 1.75–2.5.

A chemical analysis is of little use in judging the practical value of of the earth, and a practical test is necessary in order to determine its worth. An incorrect statement often seen in print is that fullers' earths contain a high magnesia-content.

Dana[1] defines fullers' earth as including many kinds of "unctuous clays, gray to dark green in color, and being in part kaolin and in part smectite." It is placed by him with several clay-like minerals (all of them hydrous silicates), namely, smectite and malthacite, of not very definite chemical composition, but all having a high percentage of combined water.

Smectite proper is defined as a "mountain-green, oil-green, or gray-green clay, from Cilly in Lower Styria."

Malthacite is defined as occurring in thin laminæ or scales, and sometimes massive, with the color white or yellowish. The original occurrence is the result of disintegration in a basalt at Steindörfel, in Lausitz. Beraum, Czechoslovakia, is another locality. It is not quite clear on what evidence Dana proves fullers' earth to be a mixture of "kaolin" (he probably meant kaolinite) and smectite, for the chemical analysis alone would not warrant this statement, and petrographic examinations (see below) thus far published afford little aid in this matter.

Indeed none of the published analyses of fullers' earth show a composition at all similar to either smectic or malthacite, and what their mineral composition is has not been proven.

Merrill[2] states that "the English earth, when examined under the microscope, consists of extremely irregular colored particles of a siliceous mineral which in its least altered state is colorless, but which in nearly every case has undergone a chloritic or talcose alteration, whereby the particles are converted into a faintly yellowish-green product. The grains are of all sizes up to 0.07 mm., but the larger portion of the material is made up of particles fairly uniform in size and about the dimensions mentioned. In addition to these are minute colorless fragments down to sizes 0.01 mm. and even smaller. The minute size of these colorless particles renders a determination of their mineral nature practically impossible, but the outline of the cleavage flakes is suggestive of a soda-lime feldspar."

"The Gadsden County, Fla., earth under the microscope shows the same greenish, faintly doubly refracting particles as does the English, intermixed with numerous angular particles of quartz."

Just what the mineralogical composition of fullers' earth is has not been definitely proven, but J. T. Porter (Ref. 11) has argued that since different writers have mentioned gabbro, diorite, diabase and basalt as rocks from which fullers' earth is derived, it is but natural to suppose that minerals common in these rocks—such as augite, hornblende, olivine, magnetite, etc.—may be present in the earth. Reasoning therefore from this basis he gives a list of sixty-two minerals which he considers are likely to be found in fullers' earth. He also lists an additional fourteen, all hydrous silicates. The presence of considerable magnesia in some earths he regards as corroborative of his theory of its source.

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[1] System of Mineralogy, 1893, p. 695.

[2] Guide to the Study of Non-metallic Minerals, p. 337, 1901.

Following out this idea, it is suggested by Porter that there may exist a well-defined relationship between the rational composition and the class of coloring matters which a given earth removes most efficiently.

The following rational compositions are given of two earths, whose ultimate analysis will be found on p. 377. Porter's calculations being based on the percentages of silica, alumina, etc., soluble or insoluble, in the different strengths of acids, but it should be remarked that the rational analysis does not balance exactly with the ultimate.

Mineral	Total	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	CO_2	H_2O	P_2O_5
OWL EARTH, FLA.									
Apatite	2.62	.....	.....	.....	1.42	.....	.....	.....	1.20
Calcite	16.82	.....	.....	.....	9.42	.....	7.40	.....	.....
Magnesite	1.01	.....	.....	.....	.....	.48	.53	.....	.....
Montmorillonite	32.04	17.21	9.70	.....	.....	.....	.....	5.13	.....
Free hydrous silica	5.46	5.00	.....	.....	.....	.....	.....	.46	
Iron oxides	.82	.....	.....	.82	.....	.....	.....	.....	.....
Magnesia (?)	1.24	.....	.....	.....	.....	1.24	.....	.....	.....
Anauxite	24.41	14.84	6.25	.....	.....	.....	.....	3.32	.....
Augite, etc	5.90	1.93	1.41	1.15	.....	1.41	.....	.....	.....
Feldspar and quartz	9.73	9.22	.44	.12	.....	.....	.....	.....	.....
	100.00	48.20	17.80	2.09	10.84	3.13	7.93	8.91	1.20
FAIRBANKS									
Apatite	.14	.....	.....	.....	.08	.....	.....	.....	.06
Free hydrous silica	11.97	11.90	.....	.....	.....	.....	.....	.07	.....
Prehnite (?)	10.16	4.43	2.54	.....	2.75	.....	.....	.44	.....
Other zeolites	2.07	.57	.....	.....	.11	1.39	.....	.....	.....
Iron oxides	2.12	.....	.....	2.12	.....	.....	.....	.....	.....
Anauxite	45.88	27.90	11.74	.....	.....	.....	.....	6.24	.....
Augite, etc	19.76	9.61	3.30	4.91	.43	1.51	.....	.....	.....
Quartz and feldspar	7.43	5.00	2.32	.11	.....	.....	.....	.....	.....
	99.53	59.41	19.90	7.14	3.37	2.90	.....	6.75	.06

Parsons (Ref. 9) gives the weight per cubic foot of fullers' earth from a number of localities in the table, p. 376.

Weight per Cubic Foot of Different Fullers' Earths

Locality	Weight per cubic foot
Summerville, Tex.	61
California	58–75
England	68
Sumter, S. Car.	36
Pikes Peak, Ga	35–40
Ellenton, Fla.	34–36
Midway, Fla.	30
Fairplay, Ark	79
Lancaster, Mass.	78

The cause of the bleaching power of fullers' earth still remains to be explained.

Both Ries and Porter have called attention to the probable presence of hydrous silica in the earth, but the second writer doubts if the bleaching power is entirely due to this, as boiling with sodium carbonate does not injure it much.

Sloan [1] believes that the bleaching is due to the mechanical entanglement of the suspended coloring matter by the contained clay substance, remarking that " when the alumina exceeds one-fifth the amount of silica present, the critical point is approximated beyond which an increase in the densely bedding aluminous matter prejudices filtration. The silica therefore serves to maintain the required porosity."

This statement regarding the alumina-silica ratio does not seem to hold true in all cases.

Porter (Ref. 11) by a series of tests on different earths has brought out their difference in behavior towards different solvents.

The results of his tests on the Owl earth from Quincy, Fla., and an earth used by the Fairbanks Company, of Chicago, are given on p. 377.

The theory advanced by him is as follows:

" 1. Fullers' earth has for its base a series of hydrous aluminum silicates.

" 2. These silicates differ in chemical composition.

" 3. They are, however, similar in all possessing amorphous colloidal structure.

" 4. The colloidal structure is of a rather persistent form, and is not lost on drying at a temperature of 130° C. or possibly higher.

" 5. These colloidal silicates possess the power of absorbing and retaining organic coloring matter, thus bleaching oils and fats.

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[1] Preliminary Report on the Clays of South Carolina, S. Ca. Geol. Surv., 1904, pp. 59–61.

ANALYSES OF FULLERS' EARTH AND CLAY

Calculated to 100 per cent *

	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	CO_2	H_2O	P_2O_5	Total
OWL FULLERS' EARTH, QUINCY, FLA.									
Original earth	48.20	17.80	2.09	10.84	3.33	7.93	8.91	1.20	100.30
Insol. in dilute HCl	74.20	12.90	1.94	.05	n. d.	.....	9.28	n. d.	98.37
Insol. in dil. HCl and NaOH	70.70	15.80	1.70	.08	n. d.	.....	9.36	n. d.	97.64
Insol. in dil. HCl and sol. in NaOH	79.72	10.52	tr.	.....	n. d.	.....	9.58	n. d.	99.82
Insol. in conc. HCl	90.88	3.40	.....	.05	.....	.....	5.14	n. d.	99.47
Insol in H_2SO_4 and NaOH	91.10	4.35	1.09	3.46	.....	.....	.....	n. d.	100.00
Insol. in H_2SO_4 and sol. in NaOH	83.17	2.81	.....	14.02	.....	.....	.....	n. d.	100.00
Sol. in NaOH alone	82.40	17.60	.....	.....	.....	.....	.....	n. d.	100.00
FAIRBANKS FULLERS' EARTH									
Original earth	59.41	19.90	7.14	3.29	2.90	.04	6.75	.06	99.49
Insol. in dil. HCl	66.60	19.20	5.54	.48	1.67	.....	7.11	n. d.	100.60
Insol. in dil. HCl and sol. in NaOH	18.80	n. d.	n. d.	n. d.	n. d.	.....	n. d.	n. d.	......
Insol. in conc. HCl	86.80	5.95	.90	.27	.27	.....	4.55	n. d.	98.74
Insol. in H_2SO_4	92.95	3.66	1.83	n. d.	n. d.	.....	n. d.	n. d.	98.44
Insol. in H_2SO_4 and NaOH	75.75	13.79	1.67	.80	n. d.	.....	n. d.	n. d.	92.01
Sol. in NaOH alone	11.89	n. d.	n. d.	n. d.	n. d.	.....	n. d.	n. d.	......

* The strength of the reagents is not given.

(" The term colloidal is used in its broadest sense to cover the whole range of conditions expressed by the words colloid, pectoid and hydrogel.")

Tests made indicate that acids affect the bleaching efficiency of some oils more than others, and in some cases bleaching may be increased by acid treatment, if the latter removes limonite, calcite or possibly hydrous alumina, which may exert a clogging effect (Ref. 11).

The injurious effect of lime on the bleaching power has also been commented upon by Parsons (Ref. 3), who also points out that the calcareous earths are not among the best bleachers.

Acid treatment may possibly increase the colloidal matter in an earth, and thus improve it.

If the different minerals in fullers' earth have a varying preference for different colors, then this may explain why certain ones are very efficient for vegetable oils, but useless for mineral oils and vice versa (Ref. 11). It is favorable to the colloid theory to note that heating the earth destroys its efficiency for bleaching cottonseed oil, and perhaps adverse to it to find that the petroleum can be burned out of the earth in kilns without injuring its bleaching power for mineral oil.

Pipe clay has some slight bleaching power, but is improved by drying and treatment with sulphuric acid, which latter increases the colloidal matter.

Parsons (Ref. 9) has brought out the interesting fact that the Southern earths are almost generally very acid in the reaction by the regular methods used in testing soils for acidity, still they contain no acid. The property is therefore simply one of adsorption such as is characteristic of many clays.[1]

This so-called " acidity " is found to be a direct measure of their absorptive capacity for such bases as lime, but it is by no means proportional to their power to extract colors from solutions in oil. This acidity Parsons found to vary from 0 in the Longstreet earth up to a point where it required 1.5 per cent of CaO to " neutralize " it in some others.

While the absorptive power is not proportional to the bleaching power of oils, it is directly proportional to the effect which many earths have of producing a rancid odor in edible oils, and this effect can be counteracted or destroyed if the earth is first treated with lime water until it no longer reacts acid to litmus paper, or gives an acid filtrate when shaken up with salt. But this treatment may at the same time destroy the bleaching power, so that only partial neutralization can be made, without endangering the value of the earth.

Strongly " acid " earths when suspended in water and subjected to the action of an electric current, acted like positively charged colloids, migrating slowly to the negative electrode, which Parsons says accounts for their yielding an acid filtrate when shaken up with salt solution, and their absorption of azo colors from an oil solution, changing them at once to the same shade as if they had combined directly with a true acid.

Some earths when mixed with oil cause the latter to oxidize so rapidly and violently in contact with the air, that the contents of the filter presses burst into flame immediately on exposure to the atmosphere.

Parsons believes that the phenomenon of bleaching is one of simple adsorption, as shown by the fact that an earth which has taken up all the color it will readily hold, yields almost all of this color to alcohol after the adhering oil has first been extracted with ether or gasoline. The earth thereby regains most of its bleaching power.

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[1] In this connection see Cameron, Bureau of Soils, Bull. 30.

With regard to the use of fullers' earth for bleaching petroleum the following facts have been noted: The longer the column of earth, the more effective the bleaching action; the coarser grained the earth, and the higher the temperature, the poorer the bleach. The oil, therefore, should be filtered at the lowest temperature at which it works well.

Treatment.—(Refs. 9 and 11.)

Minerals oils.—When petroleum is bleached, this is done by allowing the oil to flow down through columns of earth, much the same as a sugar solution is decolorized by bone black. The first oil passing out is nearly colorless, but it gradually grows darker until the earth has absorbed all the color it will remove. The earth can be revivified by burning off the adhering petroleum in rotary kilns and used again. The high heat does not appear to injure its bleaching power for petroleum oils, but would ruin the earth for use on animal and vegetable oils and fat.

Animal and vegetable oils.—For treating these the oil is heated by steam, the finely ground earth added, stirred for two or three minutes and the hot oil run into filter presses. The temperature used is variable, but commonly is not more than a few degrees below 100° C. The quantity of earth required varies with the kind of oil and earth.

Lard and lard oil generally require about 1 per cent earth; cottonseed oil about 5 per cent, and certain dark tallows and greases need much more.

After bleaching it is usually necessary to refine the cottonseed oil in order to improve its taste and odor.

A larger per cent of earth is required to reach a certain standard color if a lower temperature is used, but still this is thought by some to improve the flavor and odor.

Requisites of good earth.—Parsons names the following:

It must bleach as well as the English earth.
It must not cause the oil to revert to its original color.
It must filter well.
It must absorb no more oil than the English earth.
It must not catch fire when removed from the filter press.
It must give no permanent taste or odor to the oil.

Fullers' earth was originally used for fulling cloth, that is, cleansing it of grease, but this is now its least important application. It is also employed in the manufacture of certain soaps. Its use for removing calcium carbonate from water for boiler-supply, thus preventing deleterious incrustations, is also suggested.

Its most important use at the present time is for bleaching cotton and lard-oil, but it is also employed on castor, linseed, cocoanut and other oils, as well as on tallow and greases. Mineral oils are also filtered through it.

For filtering mineral oils the earth may be used in three sizes, viz.: through 15 on 30-mesh, through 30 on 60-mesh, and through 60 on 80-mesh (Ref. 4).

For edible oils the English earth is ground as fine as 120-mesh, but some American ones are only ground to 100-mesh (Ref. 4).

Fullers' earth has also been employed as a carrier for colors in cheap pigments used in wall paper printing, and occasionally as a bond for abrasive wheels.

Occurrence of fullers' earth in the United States.—Fullers' earth has been reported as occurring in Alabama, Arizona, Arkansas, California, Colorado, Florida, Georgia, Illinois, Massachusetts, Minnesota, Mississippi, Missouri, Nebraska, Nevada, New York, Pennsylvania, South Carolina, South Dakota, Texas, Utah, Virginia, and Washington, but in 1924 it was produced only in Alabama, Florida, Georgia, Illinois, Massachusetts and Texas.

In 1924, Georgia became the leading producer, having outranked Florida. The United States production in that year came from thirteen operators, and amounted to 177,991 short tons, valued at $2,632,432, or an average of $14.79 per ton. The imports (wrought and unwrought) for 1924 amounted to 7302 short tons, valued at $92,488.

It is interesting to note that the producers of fullers' earth are confronted with possible serious competition from certain bentonite-like materials from California, Nevada and Utah, which after treatment with sulphuric acid are said to be superior for filtering oils.[1]

Mode of Occurrence.—With the exception of the Arkansas deposits, which have been derived from basaltic dikes (Ref. 26), all of the fullers' earths of the United States are of sedimentary origin, and in their occurrence resemble deposits of transported clay. The Massachusetts material is unique in being a glacial silt (Ref. 26).

Comparatively few of the deposits have been described in detail.

Florida.—This State has for some years been the leading producer of fullers' earth. It has been worked near Quincy, Gadsden County, and Ellenton, Manatee County, the deposits in both cases being in formations of Upper Oligocene Age. The material is believed to underlie a considerable area. It has been used chiefly for bleaching mineral oils (Ref. 31).

Georgia.[2]—Fullers' earth occurs in the following three localities: (1) In the Alum Bluff formation of the Miocene, the deposits being best

[1] U. S. Bur. Mines, Min. Res., 1924.

[2] Communication from S. W. McCallie, State Geologist.

developed in the Attapulgus district along the Georgia-Florida line. The earth is light cream and brittle when dry. Its chief use is for filtering mineral oils, and it supplies probably one-third of the United States production. (2) In the Claiborne (Eocene) formation, occurring on the north edge of the coastal plain, especially in Twiggs County (Pike's Peak district). There are two beds 10–20 feet thick. It is used chiefly for vegetable oils. (3) In the Midway (Eocene) formation, found mainly in western part of State along the Chattahoochee River. The deposits, which are not worked, are similar to the Claiborne earth.

Illinois.—A deposit of fullers' earth about 30 feet thick is worked near Olmstead, Ill. It occurs in the Midway formation of the Tertiary. The earth is said to be useful for treating both vegetable and mineral oils (Ref. 27).

Alabama.—Fullers' earth has been produced for some years in Wills' Valley, 4 miles northwest of Fort Payne, De Kalb County. Some has also been produced from Tertiary beds in Clarke County (Ref. 22).

South Carolina, North Carolina, and Virginia.—Earth of very fair quality has been obtained from near Sumter, South Carolina, and deposits are also known in North Carolina and Virginia, but the earth from the last two is more or less sandy.

Arkansas.—The deposits of fullers' earth occur near Hot Springs and are derived from a dike of basic igneous rock (Ref. 26), which is said to have weathered to a depth of from 60 to 200 feet.

South Dakota.—In South Dakota (Ref. 29) the first deposits were located and opened up five miles southeast of Fairburn, Custer County, the section showing:

	Feet
Micaceous sandy clay	6
Fullers' earth	9
Micaceous sandstone	..

The earth is a yellowish gritty clay, with a somewhat nodular structure. Other deposits are known near Argyle and Minnekata. The deposits are of Jurassic age.

California.—Fullers' earth is said to occur in Kern and San Bernardino counties, but only that in the former appears to have been worked.[1] It is said to range from 15 to 50 feet in thickness. The deposits are of Cretaceous, Tertiary, and Pleistocene age.

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[1] Calif. State Min. Bur., Bull. 38, p. 274, 1906.

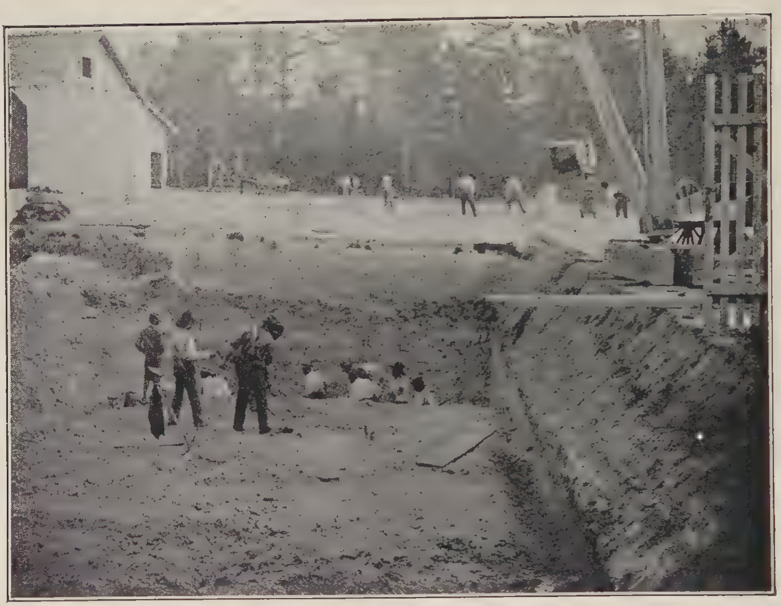

Fig. 101.—Fullers'-earth pit, Quincy, Fla. Behind it are the drying-floors. (Photo by H. Ries.)

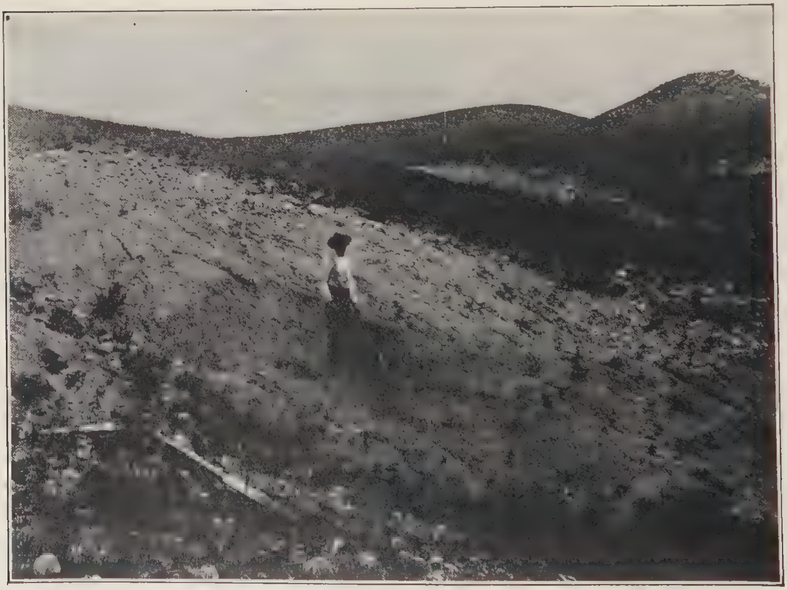

Fig. 102.—Outcrop of fullers' earth, northeast of Fairburn, S. D. (After Todd, S. Dak. Geol. Surv., Bull. 3, p. 121, 1902.)

The following table gives the composition of fullers' earth from a number of different localities:

Analyses of Fullers' Earth

	I	II	III	IV	V
Silica (SiO_2)	51.21	50.17	47.10	62.83	67.46
Alumina (Al_2O_3)	12.25	10.00	16.27	10.35	10.08
Ferric oxide (Fe_2O_3)	2.07	9.75	10.00	2.45	2.49
Lime (CaO)	2.13	0.50	2.63	2.43	3.14
Magnesia (MgO)	4.89	1.25	3.15	3.12	4.09
Potash (K_2O)	....	....	....	0.74	....
Soda (Na_2O)	....	....	....	0.20	....
Water (H_2O)	27.89	24.00	....	7.72	5.61
Moisture	....	....	15.12	6.41	6.28
Loss on ignition	....	....	5.73	....	....
Total	100.41	100.06	100.00	96.25	99.15

	VI	VII	VIII	IX	X
Silica (SiO_2)	58.72	50.36	74.90	54.32	63.19
Alumina (Al_2O_3)	16.90	33.38	10.25	18.88	18.76
Ferric oxide (Fe_2O_3)	4.00	3.31	1.75	6.50	7.05
Lime (CaO)	4.06	....	1.30	1.00	0.78
Magnesia (MgO)	2.56	....	2.30	3.22	1.68
Potash (K_2O)	2.11	....	1.75	4.21	0.21
Soda (Na_2O)					1.50
Water (H_2O)	8.10	12.05	5.80	....	7.57
Moisture	2.30	....	1.70	....	....
Loss on ignition	....	....	....	11.86	....
Total	98.45	99.10	99.75	99.99	100.74

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CHAPTER VII

DISTRIBUTION OF CLAY IN THE UNITED STATES

ALABAMA—LOUISIANA

Introduction.—In this chapter and the two following ones it is proposed to describe briefly the occurrence, properties, and uses [1] of the clays found in the different States. While it is thought that the more important facts are grouped here, still there may be some who wish to obtain additional details, which they can do by looking up the references given at the end of the discussion of each State.

A grouping of the clays according to geologic formations has been adopted partly because the subject is treated mainly from the standpoint of the economic geologist, and partly because it admits of greater uniformity in mode of presentation. For the benefit of those who would prefer a grouping by kinds, the index has been made as complete as possible, in order to enable them to find the data for which they are searching.[2]

Statistics of Production.—Doubtless few people realize the importance of the clay-working industry in the United States, and yet this is not so surprising, since clay has less popular attraction than many other mineral products, such as gold, silver, etc. A casual glance, however, at the annual figures of production will probably speedily convince one that clay is to be classed among the foremost mineral products of the country, being outranked only by coal and iron.

The statistics of production for 1923 and 1924, as published by the United States Department of Commerce, are given on the following page:

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[1] This refers to their use for the manufacture of clay-products.

[2] For a detailed bibliography of the Clay Deposits of the World, see Ries, H., Bull. Amer. Ceram. Soc., IV, p. 428, 1925.

Clay Products of the United States, 1923–24, by Products *

Product		1923		1924	
		Quantity	Value	Quantity	Value
Common brick	thousands	7,282,181	$94,472,666	7,158,714	$86,691,550
Vitrified brick or block	thousands	699,269	15,569,670	554,440	12,973,904
Face brick	thousands	1,931,175	38,891,834	2,030,403	39,931,055
Fancy or ornamental brick	thousands	12,879	252,323	538	33,419
Enameled brick	thousands	19,502	1,670,852	21,074	1,789,012
Architectural terra cotta	short tons	138,462	16,486,039	140,624	16,445,630
Fireproofing and hollow building tile	short tons	3,764,744	28,274,801	3,534,784	24,998,068
Tile (not drain)		....	23,804,157	....	24,841,813
Draintile	short tons	615,640	5,099,955	592,641	4,817,390
Sewer pipe	short tons	1,777,584	29,102,511	1,951,612	32,399,971
Stove lining	short tons	54,684	1,218,970	41,986	1,036,767
Fire brick	thousands	1,134,223	46,676,637	955,399	40,620,941
Miscellaneous		....	8,111,146	....	11,184,873
Total brick and tile		....	309,631,561	....	297,764,393
Total pottery		....	114,951,067	....	118,014,985
Grand total		....	$424,582,628	....	$415,779,378

* Figures obtained through co-operation with Bureau of the Census. Figures for 1925 not yet available.

Clay Sold by Producers in the United States, 1925

	Short tons	Value
Kaolin, china clay, and paper clay	367,319	$3,220,719
Ball clay	109,607	699,427
Slip clay	7,349	37,397
Fire clay	2,566,934	7,312,349
Stoneware clay	77,438	162,161
Miscellaneous clay	901,773	1,304,579
Total	4,030,420	$12,736,632

Although the domestic production is considerable, it is not sufficient to meet all needs, and so a considerable quantity is imported, as shown on p. 388.

Clay Imported for Consumption in the United States, 1925

	Short tons	Value
Kaolin or china clay	372,552	$3,195,694
Common blue and Gross Almerode glass-pot clay	11,889	107,940
All other clays—		
Unwrought	49,991	499,325
Wrought	2,383	29,266
Total	436,815	$3,832,225

Domestic Clay Exported from the United States, 1925

	Short tons	Value
Fire clay	44,037	$350,571
All other	39,006	530,995
Total	83,043	$881,566

ALABAMA

The clay-deposits of this State are distributed over a wide range of geologic formations, whose characters are briefly referred to below:

Archæan and Algonkian

The rocks of this age, which underlie a roughly triangular area of the eastern part of the State, consist of granites, gneisses, and schists, all of which have, by surface decay, furnished a residual clay, usually of ferruginous character. In the schist areas, however, there are not a few pegmatite veins, whose decomposition has resulted in the formation of kaolin. Such occurrences are found near Milner, Pinetucky, and Micaville, Randolph County, and Stone Hill in Cleburne County, but they are all undeveloped, owing to lack of railroad facilities. The Alabama kaolins in their crude condition are rather siliceous, highly refractory, and burn to a very white color.

Cambrian and Silurian

The clays obtained from these formations are either residual deposits or are concentrates from these, which have been carried by surface-waters down into sinks and other depressions. While the Silurian rocks contain some shaly members they are not, as far as known, used for brickmaking, but the residual clays which are usually impure are extensively employed for this purpose. At certain localities, such as at Gadsden, Kymulga, Peaceburgh, and Oaxanna, white clays occur surrounded by the impure ones, and those found in Cherokee County have been used for fire-brick manufacture.

Mississippian

Although occupying a number of small areas in the northern portion of the States no clays of economic value have been noted from this. In Will's Valley, however, it carries an important bed of white clay, which is also found farther north near the State line. The white clay, which is known locally as chalk, and has an aggregate thickness of about 40 feet, is worked near the State line about Eureka station, and thence southward for two miles.

Coal-measures

These occupy a large triangular area in the northern part of the State, but since a great portion of the region is remote from the railways, whatever shales or clays it may contain have been but little developed. The most important deposits are the under-clays found in some of the coal-fields, which have been employed for making pottery, as at Jugtown, Fort Payne, Rodentown, etc. The shales are also used in some parts of the State for making vitrified brick, especially at Coaldale and North Birmingham. No fire-clays have thus far been found in the coal-measures.

Cretaceous

This contains the most important clay-deposits in the State, but most of the beds have thus far been found in one member, namely, the Tuscaloosa. This consists usually of yellow and grayish sands, with smaller beds of pink and light-purple sands thinly laminated, dark-gray clays holding many leaf impressions, and gray lenses of massive clay which vary in color. The formation occupies a belt of country extending from the northwest corner of the State around the edges of the Paleozoic formations to the Georgia State line at Columbus, attain-ing its greatest width at the northwestern boundary of the State. The purer clays have as yet been found only in the northern part of this area, in Fayette, Marion, Franklin, and Colbert counties, and the adjoining parts of Mississippi, but the following section from twelve miles east of Tuscaloosa affords a good idea of the character of the deposits.

SECTION 12 MILES EAST OF TUSCALOOSA, ALA.

	Ft.	In.
1. Purple massive clays	5	0
2. Ferruginous sandstone crusts	6–8	0
3. Variegated clayey sands	10	0
4. Purple clays with sand partings	10	
5. Ferruginous crusts	1	0
6. Laminated, gray and yellow sandy clay	6–8	0
7. Lignite with pyrite nodules	2	6
8. Dark-gray massive clays	6	8
9. Covered	1	8
10. Purple clay	......	

This section shows great vertical variation and a similar one may occur horizontally. Nevertheless, the formation contains not a few deposits of workable size, which are employed for stoneware and common earthenware, as at Sulligent, Tuscaloosa, etc. In Colbert County the Tuscaloosa formation carries fire-clays, and other deposits are known near Woodstock and Bibbville. A curious white siliceous clay occurs near Chalk Bluff and Pearce's Mill, Marion County, but it has not been utilized.

TERTIARY

The Tertiary formations underlie the southern third of Alabama, and while it is known that they contain extensive deposits of clay, these have been but little investigated. The most promising occurrences of clay in this section are in the Grand Gulf formation (Pliocene) which, according to Dr. E. A. Smith, overlies uncomformably most of the older Tertiary beds. A siliceous clay, resembling flint-clay in appearance, is found in abundance in Choctaw, Clarke, Conecuh, and other counties. Its analysis is given in the appended table.

PLEISTOCENE

Over much of the coastal plain in the second bottoms of the rivers there is a great extent of yellow loam suitable for brickmaking, which corresponds to the Columbia loams of the Northern States.

CHEMICAL ANALYSES OF ALABAMA CLAYS

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Silica (SiO_2)	67.95	51.90	82.04	61.55	74.25	60.90	72.20	72.40	66.45	
Alumina (Al_2O_3)	20.15	35.00	12.17	20.25	17.25	18.98	17.42	14.86	18.53	
Ferric oxide (Fe_2O_3)	1.00	0.99	trace	7.23	1.19	7.68	2.40	7.64	2.40	
Lime (CaO)	1.00	0.23	trace	trace	0.40	trace	trace	0.20	1.50	
Magnesia (MgO)	trace	0.10	0.327	0.98	trace	trace	trace	0.40	1.25	
Alkalies	1.87	0.55	0.60	2.25	0.52	trace	0.56	....	trace	
Water (H_2O)	....	....	....	6.19	6.30	12.46	7.40	5.05	8.68	
Moisture	....	....	....	....	....	0.90	0.12	0.65	0.78	
Loss on ignition	8.00	11.30	4.325							

PHYSICAL TESTS OF ALABAMA CLAYS

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.
Per cent water required for mixing	37.5	25	35	20	22.6	45	33	39	26	36
Average tensile strength	143	20	5–6	40	102	100	106	55	30	100
Air-shrinkage, per cent	8	5	....	1½	6½	12.5	10	6	5	11
Fire-shrinkage, per cent	7	8	2	5	3½	6.5	4	11	10	7
Incipient fusion	2250°	2250°	2400° F.	2000°	2300°	1900°	2000°	2000°	2150°	2100°
Vitrification	....	Cone 30	Cone 27	2250°	Cone 27	2100°	2200°	2150°	2300°	2300°
Viscosity	Cone 27	....	....	....	....	2300°	2400°	2300°	2500°	Cone 27
Color when burned	cream-white	....	yellow	red	buff	red	buff	red	yellowish white	red
Plasticity	....	....	lean	moderate	good	fat	....	....	....	fair

LOCALITIES OF CLAYS IN PRECEDING TABLE

No.	Locality	Geological Age	Remarks
I	Gadsden	Cambro-Silurian	Not worked
II	Peaceburg		
III	Eureka	Mississippian	Not worked
IV	Birmingham	Coal-measures	
V	Bibbville	Lower Cretaceous	Not worked
VI	Bedford		
VII	Shirley's Mills		
VIII	Bexar		
IX	Pegram		
X	Tuscaloosa		

Numbers I–X from Bull. 6, Ala. Geol. Survey.

DIVISION OF CLAYS BY KINDS

China-clays.—The only kaolins are those occurring chiefly in Randolph County.

Fire-clays.—The fire-clays of Alabama come from four geologic horizons, namely: (1) The Cambrian and Silurian limestone formations of the Coosa Valley region, seen at Peaceburgh, Calhoun County, Oaxanna County, and Rock Run, Cherokee County; (2) the cherty limestone of the Lower Carboniferous formations of Will's Valley, seen at Will's Valley and Valley Head, DeKalb County; (3) the Tuscaloosa formation of the Lower Cretaceous, occurrences being known at Bibbville and Woodstock in Bibb County, Hull station and Tuscaloosa in Tuscaloosa County, Potter's Mills in Marion County, and Pegram in Colbert County; (4) the Lower Tertiary formation, Choctaw County.

Pottery-clays.—These are found at a number of localities, including Blount County; Rock Run, Cherokee County; Fort Payne, DeKalb County; Coosada, Elmore County; Bedford and Fernbank, Lamar County; Tuscaloosa, Shirley's Mill, Fayette County; Pegram, Colbert County.

Brick-clays.—Many deposits are found in all parts of the State.

In the table on p. 391 there are given a number of physical tests and chemical analyses of Alabama clays. Additional ones will be found in Reference 4, on p. 393.

Common brick, face brick, hollow tile, and fire brick are among the most important clay products produced in the State.

REFERENCES ON ALABAMA CLAYS

1. McCalley, H., Report on the Valley Regions of Alabama (Paleozoic strata): Clays. In two parts. I. The Tennessee Valley Region, Ala. Geol. Surv., p. 68, 1896.
2. Ibid., II. The Coosa Valley Region, p. 84, 1897.
3. Jones, W. B., Index to Mineral Resources of Alabama, Ala. Geol. Surv., Bull. 28, p. 74, 1926.
4. Ries, H., High-grade Clays of Eastern United States, U. S. Geol. Surv., Bull. 708, pp. 82, 128, 204 and 222, 1922.
5. Ries, H., The Clays of Alabama, Ala. Geol. Surv., Bull. 6, p. 220, 1900.
6. Smith, E. A., The Clay Resources of Alabama and the industries dependent on them, Eng. and Min. Jour., LXVI, p. 369, 1898.
7. Smith, E. A., Geological Relations of the clays of Alabama, Ala. Geol. Surv., Bull. 6, pp. 69–113, 1900.
8. Butts, C., Clays of the Birmingham District, Ala., U. S. Geol. Surv., Bull. 315, p. 291, 1907.

ARKANSAS

Clay-bearing formations.—Clay- or shale-bearing formations are said to occur (Ref. 2) in the Ordovician, Silurian, Devonian, Mississippian, Pennsylvanian, Cretaceous, Tertiary, and Quaternary, but only Nos. 5, 7, and 8 are regarded as important. There are also some residual clays.

Residual Clays

The bauxite deposits of Saline and Pulaski counties may be said to be of this type. With them are associated deposits of kaolin, which according to G. C. Branner are in places as much as 15 feet thick. The amount of overburden varies and the kaolin has not been used.

Mississippian

The Fayetteville formation of the Mississippian contains a soft shale up to 150 feet thick, which is well developed along the West Fork of the White River near Fayetteville, and is said to be suitable for brickmaking. Many beds of shale are found in the Coal Measures of the Pennsylvanian, but their value is not known. According to Branner (Ref. 2) they occur in great abundance between Little Rock and Fort Smith.

Cretaceous

The Cretaceous occurs only in a small area in the southwestern corner of the State and is said to contain no clays of commercial importance, although " sedimentary " kaolins have been reported from Pike County (Ref. 2).

TERTIARY

Tertiary clays underlie a large part of the State east and south of the St. Louis, Iron Mountain and Southern Railway, as well as along the lowest part of Crowleys Ridge. Branner states that beds of fire-clay occur with lignite in the Crowleys Ridge region.

An interesting clay of the glass-pot type has been worked at Lester, Ouachita County, and the following tests of a washed sample, made by the U. S. Bureau of Mines show its qualities.

Workability: very smooth.

	Per cent
Water of plasticity	29.73
Volume air shrinkage	26.19
Linear air shrinkage	9.50

		Pounds per square inch
Modulus of rupture,	Raw clay	1068.6
	1 clay : 1 sand	405.1

FIRE TESTS

Temperature, ° C.	Porosity, per cent	Color	Volume shrinkage, per cent	Linear shrinkage, per cent
1190	18.70	Light buff	3.20	1.20
1250	19.19	Deep cream	4.52	1.80
1310	20.45	Light buff	4.11	1.61
1370	17.50	Deep buff	2.90	1.01
1410	13.90	Deep buff	3.50	1.33

Fusion point, cone 26. Steel hard, 1190° C.

Common pottery clays of variable quality and thickness are said to occur in the Lower Tertiary in several counties.

On the Hotsprings (Ref. 3) reservation the Paleozoic shales have, by decay and leaching in place, yielded a series of light-colored siliceous clays. They form beds of variable thickness, sometimes interbedded with sandstones. These clays have been worked outside the reservation on Cedar Mountain, near Mountain Valley P. O., and shipped to Chicago for use in making art pottery. Only analyses are available, and these give little information regarding their physical properties:

	I	II
Silica (SiO_2)	70.31	74.55
Alumina (Al_2O_3)	17.27	13.68
Ferric oxide (Fe_2O_3)	1.35	1.27
Lime (CaO)	.23	.20
Magnesia (MgO)	.91	2.03
Potash (K_2O)	3.51	3.84
Soda (Na_2O)	.26	.10
Titanic acid (TiO_2)	1.00	.73
Ignition	4.36	3.63
Moisture	.88	.77
	100.08	100.80

Quaternary deposits occupy a large area in the southern and eastern part of the State. The clays of this age which have been worked occur on and near Crowleys Ridge, which extends from the north boundary of the State in Clay County, south through Phillips County. The clays of this region are said to be of two kinds, viz.: (1) Loess, which occurs

Analyses of Arkansas Clays

	I	II	III	IV	V	VI	VII	VIII	IX
Silica (SiO_2)	53.30	62.36	58.43	51.30	63.07	48.34	76.33	75.99	45.28
Alumina (Al_2O_3)	23.29	25.52	22.50	24.69	23.92	34.58	16.04	16.12	37.39
Ferric oxide (Fe_2O_3)	9.52	2.16	8.36	10.57	1.94	1.65	1.24	1.35	1.71
Lime (CaO)	.36	.51	.32	.32	.23	.81	By diff. .99	1.45	1.83
Magnesia (MgO)	1.49	.29	1.14	.63	tr.	tr.			.29
Potash (K_2O)	1.36	1.90	2.18	2.18	1.15	.44			.....
Soda (Na_2O)	2.76	.66	1.03	.72	1.08	1.26			.....
Water (H_2O)	5.16	5.32	6.87	9.11	7.07	12.94	5.40	......	13.49
Total	97.24	98.72	100.83	99.52	99.46	100.02*	100.00	94.91	99.99

* TiO_2 1.56.

I. Clay-shale from railroad cut at south end of upper bridge, Little Rock.
II. Decayed shale from Iron Mountain Railroad cut, at crossing of Mt. Ida road, Little Rock.
III. Clay-shale from Nigger Hill, Little Rock.
IV. From S. E. ¼ of S. W. ¼, Sec. 31, 10 N., 23 W.
V. Benton, Hick's bed, 2 S., 15 W., Sec. 12.
VI. Benton, Howe's pottery.
VII. John Foley's, 13 S., 24 W., Sec. 18, N. E. ¼ of S. E. ¼.
VIII. Climax pottery, 15 S., 28 W., Sec. 5, W. ½ of S. E. ¼.
IX. Kaolin, 1 N., 12 W., Sec. 36, Tarpley's.
I–IV, Carboniferous; V–IX, Tertiary. Branner, Ref. 1.

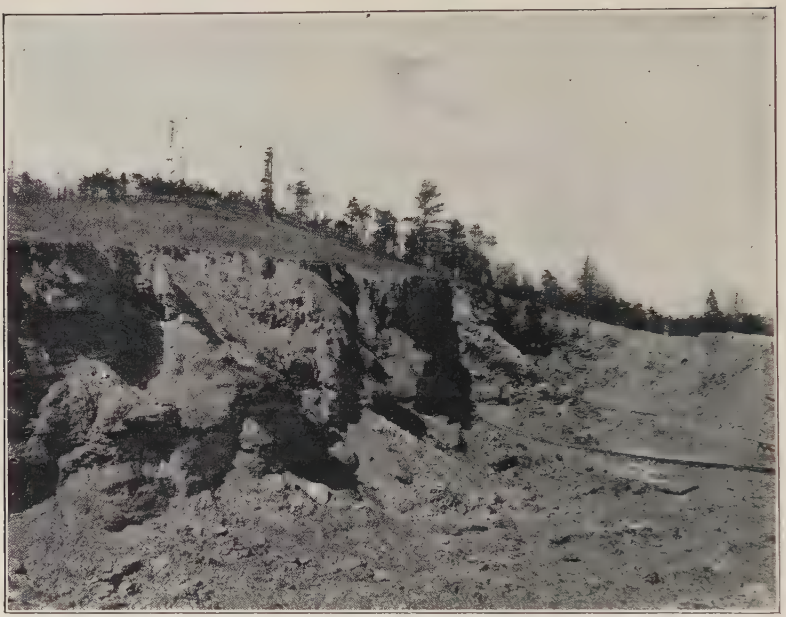

FIG. 103.—Pit of Carboniferous shale near Birmingham, Ala. (Graves photo.)

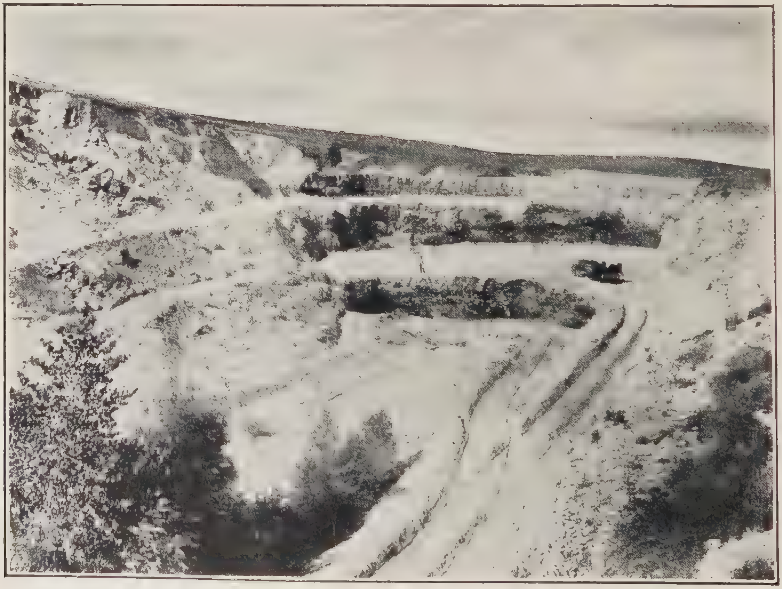

FIG. 104.—Tertiary clays (Ione formation) used for brick, terra-cotta, etc., Lincoln, Calif. (Photo loaned by Gladding, McBean & Co.)

on the ridge and on the hill slopes, some of it which is suitable for brick being used. (2) Buckshot clay, a light gray sandy clay with abundant small limonite nodules. This occurs all over the low country for fifty miles or more west of Crowleys Ridge. There are some smaller areas of it east of the ridge. Common brick have been made from it at several localities, but the product is spotted on account of the nodules.

Uses of Arkansas clays.—Common brick have been made at many localities, mostly at small plants, and for local use. Paving brick have been made at Fort Smith. There has been a small production of stoneware at several localities.

REFERENCES ON ARKANSAS CLAYS

1. Branner, J. C., Cement Materials of Southwestern Arkansas, Trans. Amer. Inst. Min. Engrs., Vol. XXVII, p. 42, 1897.
2. Branner, G. C., The Commercial Clays of Arkansas, The Ceramist, VII, p. 250, 1906.
3. Branner, J. C., The Clays of Arkansas, U. S. Geol. Surv., Bull. 351, 1918.
4. Annual Report of State Geologist for 1888, Pt. V, p. 11. Gives numerous analyses.
5. Eckel, E. C., Clays of Garland County, Ark., U. S. Geol. Surv., Bull. 285, p. 407, 1906.
6. Purdue, A. H., Possibilities of the Clay Industry of Arkansas, Ark. Brickmakers Assoc., Little Rock, 1910.
7. Ries, H., High Grade Clays in Arkansas, U. S. Geol. Surv., Bull. 708, pp. 120–121, 255–259, 1922.

ARIZONA

The clay resources of this State have been but little developed.

Ransome[1] states that clay for use in a mixture to line converters is obtained from near the Czar fault in the Copper Queen mine, and has been formed by decomposition or alteration of the Obrigo limestone.

Common brick-clays are used locally at a few points.

CALIFORNIA

Published information regarding the properties of the California clays is very meager, although many scattered references are to be found in the annual reports of the California State Mineralogist, especially the 7th to 13th.

Residual clays are derived from many of the formations occurring within the State, and are occasionally worked for common brick.

Of the sedimentary clays, those belonging to the Ione formation of the Neocene, extensively developed in the Great Valley, are the most important, but unfortunately they are exposed in only a few places.

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[1] U. S. Geol. Atlas, Folio No. 112, p. 17.

Lindgren[1] states that the white clays of this formation are frequently well suited to pottery manufacture, and the clay industry has been extensively developed around Lincoln, Placer County. Similar beds are found at many places in the Cosumnes area, but they are not worked.

The white Ione clays have also been extensively dug to the northwest of Ione and above Carbondale, to be used in making coarse pottery. A variegated clay of good quality has been quarried at Valley Springs and shipped to Stockton for making pottery.[2]

A belt of clays is also said to extend in a general west of north and east of south direction from Elsinore on the south to Corona on the north. These have been dug for the factories at Elsinore, Corona, and Los Angeles (Ref. 1).

At Los Angeles the Tertiary clays are used locally for brick and flower-pots.

The Lincoln locality, although the smallest of the three important ones, is extensively worked; the Carbondale area contains probably the best grades of clay, but the Elsinore-Corona belt affords a greater variety.

At Alberhill, seventy miles southeast of Los Angeles, much high-grade clay is obtained from Tertiary deposits (Ref. 4). The main stratum known as M. T. clay fires to a light cream color and fuses at cone 29. Another bed yields a smooth plastic blue clay, whose fusion-point is cone 32 and which is used in the manufacture of face brick, terra-cotta, stoneware and other pottery. Still a third is classed as ball-clay, and a fourth which is non-plastic, white and highly refractory makes, when calcined, a good grog for fire-brick (Ref. 3). Some bauxites also occur.

The clay products of California include common, and pressed brick, hollow blocks, sewer-pipe, drain tile, terra-cotta, roofing- and floor-tile, porcelain, stoneware and other pottery.

REFERENCES ON CALIFORNIA CLAYS

1. Anon., Industrial Materials of California, Cal. St. Min. Bur., Bull. 38, 1903.
2. Boalich, E. S., and others, The Clay Industry of California, Cal. St. Min. Bur., Prelim. Rept., No. 7, 1920.
3. Burchfield, B. M., Refractory Clays of the Alberhill, California Deposits, Jour. Amer. Ceram. Soc., VI, p. 1167, 1923.
4. Johnston, W. D., Clays, Cal. State Mineralogist, 9th Ann. Rept., p. 287, 1890.
5. Ries, H., The Clayworking Industry of the Pacific Coast, Mines and Minerals, Vol. XX, p. 487, 1900.

COLORADO

The clay-bearing formations include the Permian-Triassic (?), Jurassic, Comanchean, Cretaceous, Tertiary and Quaternary.

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[1] U. S. G. S., Geol. Atlas, Folio 5.

[2] Turner, U. S. Geol. Survey, Geol. Atlas, Folio 11.

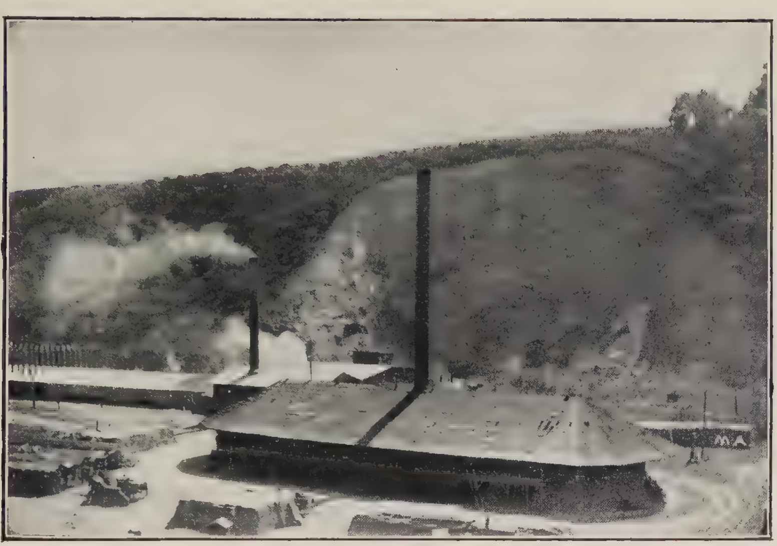

Fig. 105.—Tertiary clays used for common brick, Los Angeles, Calif. (From Bull. 38, Calif. State Min. Bur.)

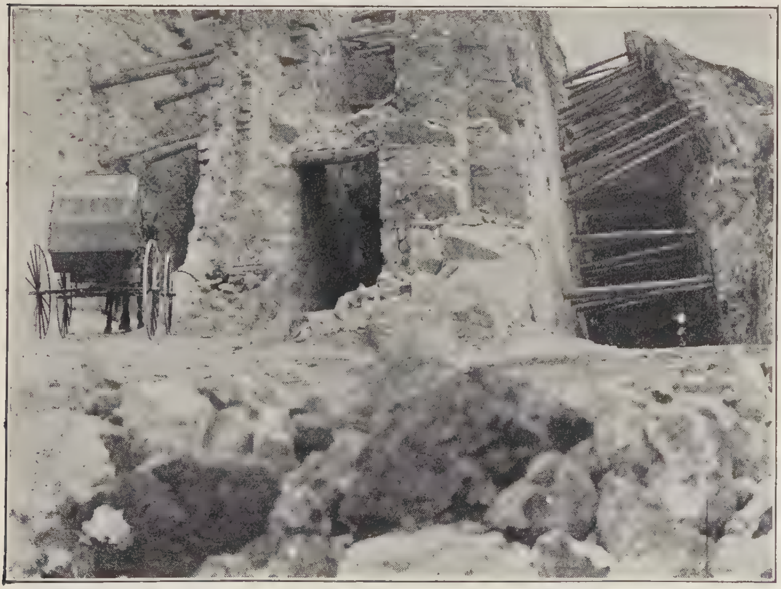

Fig. 106.—View of fire-clay pits, Golden, Colo. The good clay has been taken out, the worthless sandy beds left standing. (Photo by H. Ries.)

Clays from all these (Ref. 7) have been examined and tested, but have not all been developed commercially.

PERMIAN-JURASSIC

The Upper Wyoming series of the Permian-Triassic shows its greatest development near Boulder but the shales are usually too sandy and too high in iron to be of any value, though some may do for common brick.

The Marion formation of the Jurassic carries some low-grade shales that might be used for common brick, but other beds are highly calcareous.

CRETACEOUS-TERTIARY

In the upper part of the Purgatory formation of the Comanchean there are white-burning refractory clays and shales, while some ball-clays are also said to occur.

The Cretaceous and Tertiary beds are well exposed along the eastern edge of the Rocky Mountains, where they have been worked for some years.

The Dakota formation which has been worked, especially in the Denver basin and also around Park City and Canon City, has lenses of clay and shale up to 10 feet in thickness. At times the beds have been found too thin to exploit, but around Golden a considerable quantity of clay has been obtained from the hogbacks.

These Dakota clays have been found adapted to a rather wide variety of uses, including fire-brick, common brick, assayers' crucibles, earthenware, etc.

The distribution of the Dakota formation is shown in the U. S. Geol. Atlas Folio sheets; 36, Pueblo; 68, Walsenburg; 135, Nepesta; and in U. S. Geol. Surv., Prof. Pap. 32.

The shales of the Graneros and Carlisle formations (Benton) are said to be suitable for making a good quality of common red brick, and around Golden they were formerly used for stoneware and sewer-pipe. This shale has also been worked at La Junta for dry-pressed brick.

The clays in the western and southwestern part of the State have received but little attention. In the Durango-Gallup coal-field area heavy clay shale deposits occur in the Mancos and Lewis formations of the Upper Cretaceous, and thinner beds in the Mesaverde and Laramie formations, but the first two include the greater part of the thick shale formations of the area. The Mesaverde formation also carries semi-refractory fire-clays associated with the coals and sand-stones.

The Mancos shale has been used for pressed brick at Durango. It burns red, but contains limestone concretions which have to be removed in quarrying. Its analysis is given in the table on p. 401.

The Mesaverde fire-clays occur in the coal measures between Durango and Mancos, as do also the Mancos shales. In Rages Basin, southwest of Durango, there are thick outcrops of the Lewis shale, and it is continuously exposed (but not worked) as far as the La Plata River in the vicinity of Fort Lewis.

In the Pierre formation which is from 1250 to 7900 feet thick, there are mostly low grade brick shales. These have been worked at Boulder, and have been used for common, pressed, and paving brick.

TERTIARY

The Dawson formation which has a maximum thickness of 2000 feet and covers a large area between Colorado Springs and Denver, contains lenses of clay interbedded with sandstone and conglomerate. Many of the clays are said to be true fire-clays, while others may be suitable for fire-brick.

PLEISTOCENE

The loess is used at many points in eastern Colorado for making common brick, and many brick-yards around Denver are supplied with it. At other localities alluvial clays are easily obtained.

ANALYSES OF COLORADO CLAYS

	I	II	III	IV	V	VI
Silica (SiO_2)	50.35	63.309	46.61	63.22	48.87	76.56
Alumina (Al_2O_3)	33.64	14.38	37.20	24.72	12.26	8.30
Ferric oxide (Fe_2O_3)	.75	6.27	.15	.43	4.44	.38
Ferrous oxide (FeO)	......	.859	......	......	.07	......
Lime (CaO)	......	1.81	.44	.30	10.06	.12
Magnesia (MgO)	trace	2.57	.25	.13	3.82	.24
Potash (K_2O)	.49	1.28	1.23	trace	1.76	trace
Soda (Na_2O)	.09	2.19			.55	
Titanic acid (TiO_2)	.80	......	......	.68	......	.60
Water (H_2O)	11.75	5.223	13.65	8.63	16.39†	4.40
Moisture	2.13	2.05	.47	1.36	1.27	1.26
Organic matter	......	......	......	.40	.45‡	8.31
Total	100.00	99.941	100.00	99.87	99.94	100.17

† Includes CO_2. ‡ SO_3.

I. A typical Golden fire-clay, U. S. G. S., Mon. XXVII, p. 390.
II. Pierre shale, Lee yard, Boulder County, U. S. G. S., Bull. 265, p. 74.
III. Edgemont, Jefferson County, } U. S. G. S., 16th Ann. Rept., Pt. IV, pp. 554–565.
IV. Pueblo, Pueblo County }
V. Durango. U. S. G. S. Bull. 315, p. 296, 1906.
VI. Dakota fire-clay, Nepesta quadrangle. U. S. Geol. Atl. Folio, 135.

The following physical tests of a few selected clays are from Butler's report (Ref. 1):

PHYSICAL TESTS OF COLORADO CLAYS

	I	II	III	IV	V	VI
Water plasticity, per cent	31.7	25.7	31.4	35.4	23.6	19.1
Linear air shrinkage, per cent	9	9	6	9	6	4
Tensile strength, pounds per square inch	14	121	43	86	121	53
Incip. vitrification, cone	3	010	010	05	03	01
Fire shrinkage at incip. vitrif., per cent	6	1	5	3	2	3
Absorption at incip. vitrif., per cent	5.0	10.0	3.7	12.3	19.4	13.5
Color	flesh	lt. pink	red	flesh	white	red
Fusion point, cone	12	3	18	12	30+	3

I. Shale, Laramie formation, Boulder.
II. Clay, Pierre formation, Boulder.
III. Sandy clay, Dawson formation, Douglas Co.
IV. Shale, Graneros formation, El Paso Co.
V. Fire-clay, Dawson formation, El Paso Co.
VI. Brick-clay, Mesa Co.

REFERENCES ON COLORADO CLAYS

1. Butler, G. M., Clays of Eastern Colorado, Colo. Geol. Surv., Bull. 8, 1914.
2. Geijsbeek, S., Colorado Clays, Clay Worker, XXXVI, p. 424, also Whiteware Possibilities of Colorado Raw Materials, Trans. Amer. Ceram. Soc., Vol. VIII, p. 98, 1906.
3. Shaler, M. K., and Gardner, J. H., Clay Deposits of the Western Part of the Durango Gallup Coalfield of Colorado and New Mexico, U. S. Geol. Surv., Bull. 315, p. 296, 1906.

CONNECTICUT

The clays at present worked in this State are confined to the central lowland portion of the State. Kaolin was formerly worked at West Cornwall in Litchfield County.

RESIDUAL CLAYS

At West Cornwall, Litchfield County, there is a deposit of kaolin, which has been formed by the weathering of a bed of feldspathic quartzite, but has been protected from glacial erosion, partly because of its location in a hollow, and partly because of its being interbedded with harder quartzites. It is of white color, and sandy or granular texture. The deposit, which has a length of at least 1000 feet, dips southeastward at a rather steep angle and was worked by forcing water down through pipes and washing out the clay, which was then brought up in suspension and floated down to the settling-tanks. This clay was sold to potters and paper manufacturers. An analysis of the washed material is given below.

PLEISTOCENE

Nearly all of the workable clay-deposits of Connecticut are of this age, and were deposited either in estuaries at a time when the land stood at a lower level, thus allowing the water to occupy some of the valleys entering Long Island Sound, or else they were laid down in lakes, formed by the damming of the valleys by glacial drift. The valley of the Quinnipiac depressed below sea-level, became a long, deep estuary in which the fine clay derived from the material in and under the ice was deposited.

The Milldale, Berlin, Middletown, and Cromwell clays are lake-deposits.

The central Connecticut clays are grouped by Loughlin (Ref. 1) into five areas, as follows:

Northern area, the largest in the State and including the brick-yards in and north of Hartford. The clay is a blue or sometimes red deposit of highly plastic character, alternating with layers of fine quicksand.

This area extends from King's Island to eastern Rock Hill County. At Hartford it lies chiefly west of the river and is four to five miles in width, thence it extends northeastward to South Windsor, where east of the river its width is two to five miles. Its thickness varies from a few feet to as much as 95. At most points the clay is overlain by a varying thickness of red or yellow sand.

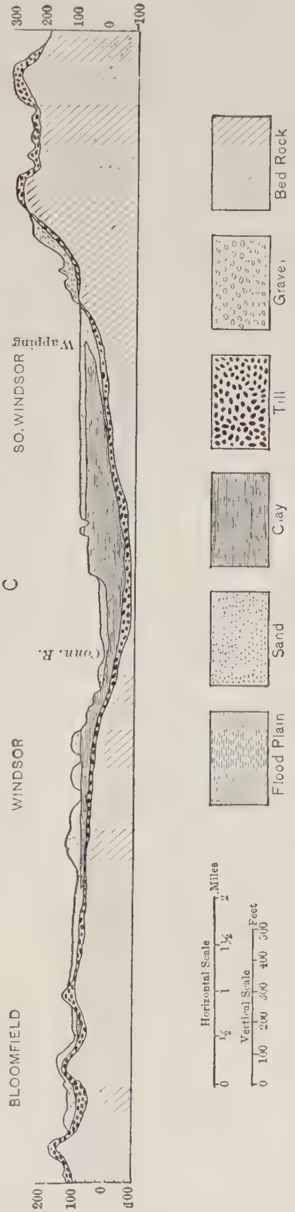

FIG. 107.—Section across Connecticut Valley, showing relations of the clays and other Pleistocene deposits. (After Loughlin, Conn. Geol. and Nat. Hist. Surv., Bull. 4, p. 12, 1905.)

Clayton area, a small area of reddish clay, having a depth of not less than 15 or 20 feet and overlain by coarse sand.

Berlin area, a brownish-red clay-deposit in the valley of the Sebeth River between Berlin and Middletown.

Quinnipiac area, including the clays extending from North Haven southward into New Haven. The clay is similar to that of the Berlin region, and is usually overlain by several feet of peat. Its measured thickness ranges from 6 to 30 feet.

Milldale area. This is the smallest of the worked deposits. In character the material is similar to the others.

All of these Pleistocene clays are used chiefly for the manufacture of common brick, although a small quantity of the drain-tile and earthenware is also produced. The stoneware and fire-brick manufactured in Connecticut are from New Jersey clays.

The following analyses are taken from Loughlin's report referred to below:

ANALYSES OF CONNECTICUT CLAYS

	I	II	III	IV	V	VI
Silica (SiO_2)	47.50	52.73	50.33	55.27	58.02	56.75
Alumina (Al_2O_3)	37.40	22.25	27.06	20.52	17.93	17.54
Ferric oxide (Fe_2O_3)	0.80	3.14	2.29	5.34	4.89	4.92
Ferrous oxide (FeO)	....	4.55	2.62	1.55	1.24	0.93
Lime (CaO)	trace	1.48	1.22	2.21	3.42	4.18
Magnesia (MgO)	....	3.20	3.34	2.80	1.92	2.34
Soda (Na_2O)	1.10	2.22	1.78	2.82	3.33	3.40
Potash (K_2O)		4.28	4.40	3.43	3.06	3.16
Water (H_2O)	12.48	1.12	1.42	1.37	0.99	1.24
Moisture	....	4.91	5.24	5.06	5.36	6.28
Clay substance	99.00	....	....	....	....	....
Quartz	1.00	....	....	....	....	....
Clay base	....	34.15	47.36	34.04	28.75	27.82
Non-fluxing impurities	....	46.86	36.69	48.18	53.55	53.99
Fluxes	....	18.87	15.65	18.15	17.86	18.93

I. West Cornwall, kaolin, H. Ries, analyst.
II. S. Windsor, Conn., East Windsor Hill Brick Co.
III. Newfield, Tuttle Bros.
IV. Berlin, Berlin Brick Co.
V. North Haven, I. L. Stiles & Sons.

REFERENCES ON CONNECTICUT CLAYS

1. Loughlin, G. F., The Clays and Clay Industries of Connecticut, Conn. Geol. and Nat. Hist. Surv., Bull. 4, 1905.

2. Sheldon, J. M. A., Concretions from the Champlain Clays of the Connecticut Valley, 45 pp.; 1900, Boston, Mass.; Abstracted in Amer. Jour. Sci., 4th ser., Vol. XI, p. 397, 1901.

DELAWARE

The clay resources of this State are of comparatively little importance, nor has much been published regarding them. In the northwestern part, along the Pennsylvania boundary, there are deposits of kaolin similar to those found in southeastern Pennsylvania. The product is washed before shipment.

The Potomac beds of the coastal plain area are said to contain stoneware and fire-clays, which have been dug at two localities not far from Wilmington.

DISTRICT OF COLUMBIA

According to Darton[1] there is an abundance of brick-clay around Washington and much of it is used, in fact large areas have been dug over in the immediate vicinity of the city. The materials employed are chiefly loams belonging to the Columbian formation, but the sandy clays of the Potomac beds are also used.

FLORIDA

The clays of Florida are mostly surface deposits of Tertiary and Pleistocene age.[2]

Tertiary

Residual clays from the Ocala limestone (Eocene) are found at a number of localities, especially along the Gulf side of the northern part of the peninsula. They are of variable character but some could be used for common brick. The Chattahoochee formation (Oligocene) also yields residual clays some of which are calcareous but none are at present used. Similar ones are derived from the Tampa limestone. A sedimentary clay occurring in the Tampa formation was formerly used for brick.

The Alum Bluff Formation (Miocene) which is one of the most widely distributed of the exposed formations in Florida, carries sands, clays and fullers' earth. Other Tertiary formations are also clay-bearing.

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[1] U. S. Geol. Atlas, Folio No. 70, Washington, D. C.

[2] For distribution of the geologic formations see map accompanying 14th Ann. Rept., Florida Geol. Surv., 1922.

The most valuable clay found in Florida is the so-called sedimentary kaolin, a white sedimentary clay occurring at a number of localities in the peninsular portion of the state. The exact position of this deposit in the Tertiary formations is not definitely settled.

The crude material may be described as a whitish clay-bearing sand, ranging from 6 to over 30 feet in thickness, and underlain by an impure clay. The clay has to be washed before shipment to market, and this is being done at Edgar and Okahumpka.

A chemical analysis of the washed material is shown in the table, p. 407.

The following physical tests of the washed clay were made by the Bureau of Mines at Columbus, Ohio:

PHYSICAL TESTS OF FLORIDA WHITE CLAY

Workability: very plastic; molds well.

	Per cent
Water of plasticity, in terms of dry clay	49.78
Air shrinkage, measured by volume	32.15
Air shrinkage, linear, calculated	12.20
Modulus of rupture, pounds per square inch	181

FIRE TESTS

Temperature, ° C.	Porosity, per cent	Color	Volume shrinkage, per cent, in terms of dry clay	Linear shrinkage, per cent, in terms of dry clay
1190	28.3	white	32.1	12.1
1250	27.05	cream white	33.11	12.5
1310	23.41	cream white	37.33	14.4
1370	7.4	cream	46.3	18.7
1410	2.2	buff	49.4	20.3

The washed product is widely used in the manufacture of whiteware industries, for making pottery, wall- and floor-tile, electrical porcelain, etc., but not alone. The refuse sand from the washing process has been used to some extent for concrete work.

PLEISTOCENE—RECENT

Many alluvial and lacustrine deposits of clay are scattered throughout the State. Some of these clays have been worked, but others are undeveloped. They are adapted to the manufacture of brick and tile.

ANALYSES OF FLORIDA CLAYS

	I	II	III	IV
Silica (SiO_2)	35.95	30.83	46.11	45.39
Alumina (Al_2O_3)	13.23	15.40	39.5	39.19
Ferric oxide (Fe_2O_3)	1.27	1.40	.35	.45
Lime (CaO)	15.00	13.78	....	.51
Magnesia (MgO)	5.40	7.50	.13	.29
Alkalies (Na_2O,K_2O)	....	undet.	....	.83
Water (H_2O)	10.55	7.16	13.78	14.01
Carbon dioxide (CO_2)	18.50	20.14	....	....
Sulphur trioxide (SO_3)	....	....	.07	....
Total	99.90	96.21	99.94	100.67

I. Calcareous clay, Leon County, H. Ries, analyst.
II. Calcareous clay, near Jackson Bluff on Ocklocknee River, H. Ries, analyst.
III. Washed clay from Palatlakaha River.
IV. Washed clay from Edgar, C. Langenbeck, analyst.
I–IV from U. S. Geol. Surv., Prof. Pap. 11, p. 83.

PHYSICAL TESTS OF SOME FLORIDA CLAYS

	I	II	III
Water plasticity, per cent	29.45	27.45	29.75
Linear air shrinkage, per cent	8.30	11.5	9.7
Modulus of rupture, pounds per square inch	570.9	400.2	421.7
Steel hard cone	05	....	1
Color fired	cream	pink to brown	red

Temperature, ° C.	I		II		III	
	Linear fire shrinkage	Porosity	Linear fire shrinkage	Porosity	Linear fire shrinkage	Porosity
950	2.7	35.60	0.5	33.2	0.3	34.0
1050	3.2	36.00	0.5	33.6	0.3	34.6
1150	6.7	25.20	1.0	32.4	7.3	26.2
1190	6.7	19.30	1.0	30.2	7.3	18.5
1230	6.7	15.80	1.0	29.4	7.3	16.8
1310	6.7	10.60	1.0	30.1	7.8	16.4
1370	7.2	6.70	....	....	7.8	13.1
1430	8.2	3.65	....	....	7.8	14.4

I. Estiffanula Bluff, Liberty Co. Cream burning bottom clay. Not worked.
II. Campville, Alachua Co. Yellowish-brown burning brick clay.
III. Blountstown, Calhoun Co. Red-burning brick clay.
I–III from Fla. Geol. Surv., 15th Ann. Rept., 1924.

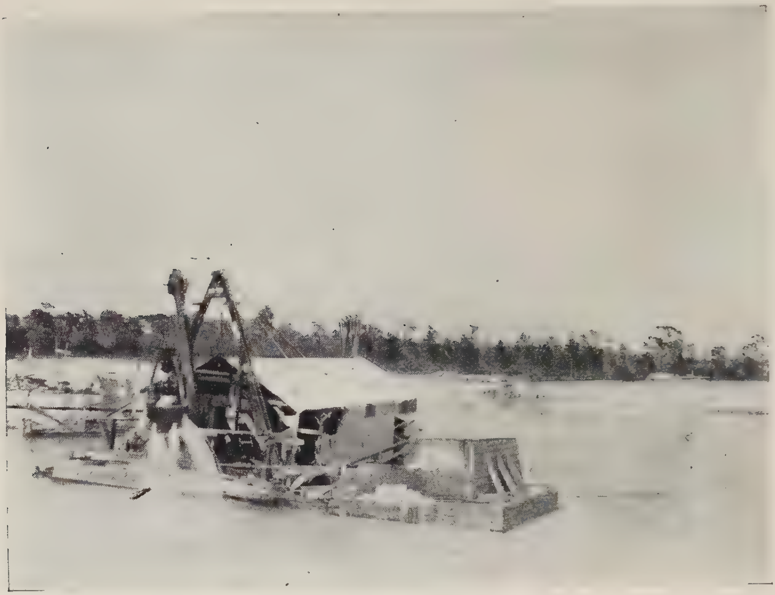

FIG. 108.—Dredging white clay near Edgar, Fla. (H. Ries, photo.)

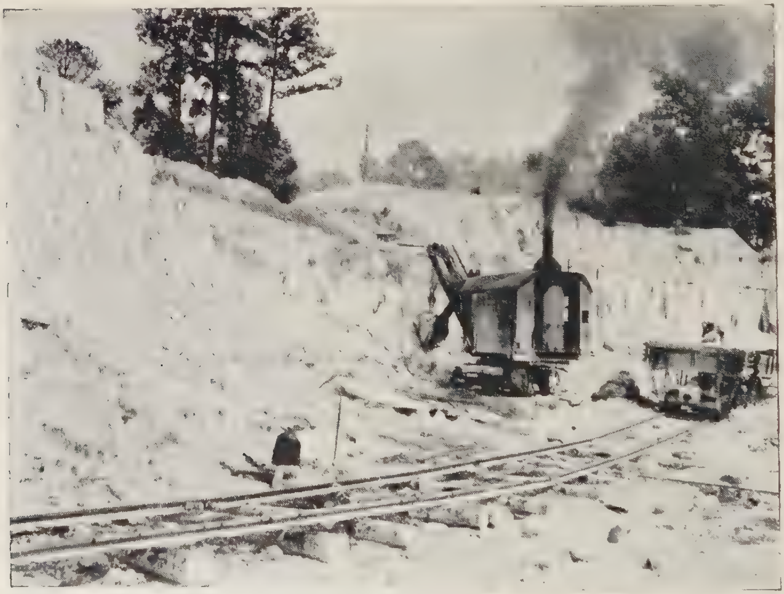

FIG. 109.—Mining white Cretaceous clay near McIntyre, Ga. (H. Ries, photo.).

No clays suitable for vitrified brick appear to have been found in the State. The clay products are chiefly building brick, drain-tile, and red earthenware.

REFERENCES ON FLORIDA CLAYS

1. Bell, O. G., Preliminary Report on the Clays of Florida, Fla. Geol. Surv., 15th Ann. Rept., pp. 53–260, 1924.
   Contains complete bibliography of all preceding publications.

GEORGIA [1]

This State is divisible geologically into three areas, namely: (1) A northwestern area, underlain by shales, limestones, and sandstones of Paleozoic age. (2) A broad central belt of Pre-Cambrian rocks, such as granites and gneisses. (3) A southern belt, in the coastal plain region, composed largely of unconsolidated sedimentary rocks of Cretaceous, Tertiary, and Pleistocene age.

Pre-Cambrian Belt

This covers an area of about 12,000 square miles, and consists of granites, gneisses, schists, marbles, and in places pegmatite veins, of which the last should afford kaolin. Residual clays are abundant throughout the region, and the wash from them may form secondary deposits in the valleys. Face and common brick are made from these clays at a number of localities.

Paleozoic Area

This belt includes the counties of Polk, Floyd, Bartow, Gordon, Murray, Whitfield, Catoosa, Chattooga, Walker, and Dade.

The rocks in this area range from Cambrian to Carboniferous inclusive. The shales are often calcareous, with the exception of the Carboniferous ones. The residual clays derived from these formations are not all alike, are often of considerable extent and generally of ferruginous character. They are chiefly adapted to common and face-brick manufacture, but there are local areas of bauxite and refractory clays near Rome, which are well adapted to the manufacture of refractory products. The residuals from the limestones often contain chert nodules.

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[1] Much recent information regarding the clays of this State has been supplied by Prof. S. W. McCallie, Dr. Henry, and Mr. R. W. Smith.

COASTAL PLAIN REGION

This region includes that portion of the State lying to the southeast of a line drawn through Augusta, Macon, and Columbus, and coinciding approximately with the fall line (Fig. 110).

Within this area the formations range from Cretaceous to Pleistocene and carry clay deposits of variable character.

Of these the most important are those of the Upper Cretaceous. These occur along the northern border of the Coastal Plain in a strip 220 miles long, and forty to fifty miles wide, which is known as the Fall Line Hills.

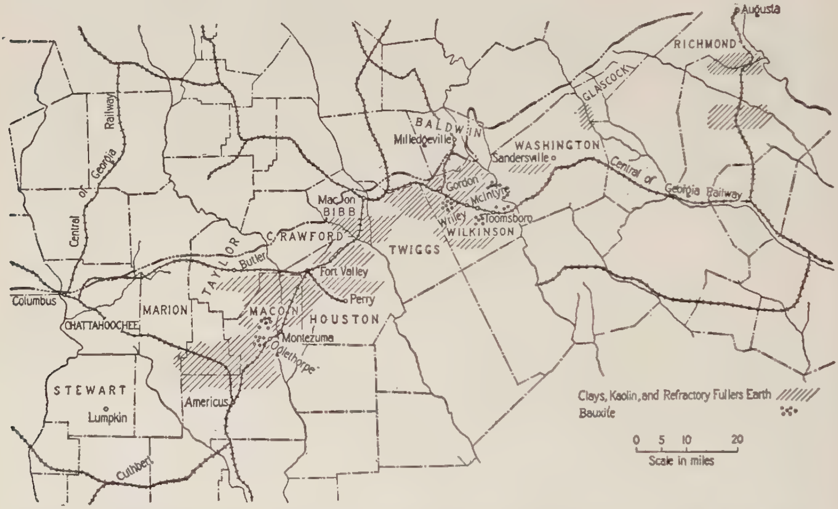

FIG. 110.—Map of white sedimentary kaolin areas of Georgia. (U. S. Bur. Mines, Bull. 252, 1926.)

The important deposits belong to the Middendorf formation of the Upper Cretaceous (C. W. Cooke), and are supposed to be of the same age as the fire-clays of New Jersey.

The Upper Cretaceous deposits rest unconformably on the crystalline rocks, and are in turn overlain uncomformably by Eocene or later formations.

The overburden of the clays ranges from 4 to 40 feet in thickness.

"The Upper Cretaceous outcrop and the adjoining area covered with thick overburden form an area of twenty to thirty miles wide, which extends across the State in a southwest direction from Augusta to Columbus. Within this area the beds of sedimentary kaolin and bauxite lie near the surface and mining can be done at a low cost."

The white clays and associated refractory ones occur as lenses which may vary in size from small ones only a few inches in thickness and an acre in extent, to others which are over 40 feet thick and may have an area of over a square mile.

No less than six types of material are found, whose names and characters are as follows:

1. Flint clays, of local importance, having a conchoidal fracture and developing little plasticity when finely ground. They show practically no fire-shrinkage below cone 12 and deform at cones 31 to 33. Used to limited extent in refractories.

2. Hard clays. Light cream to white in color, and burning buff or white. Fine grained, plastic and of good bonding strength, with deformation temperatures of cone 33 to 35. Occur as lenses, sometimes of considerable size, and offer a good material for refractories. Hardness due to free silicic acid (Ref. 9).

3. Soft clays. Cream to light blue, firing cream to white. Of low bonding strength but good refractoriness. When used to extent of over 30 per cent in plastic bodies they are liable to crack in drying but work satisfactorily in dry press bodies for floor- and wall-tile, and electric insulators.

4. Semi-hard clays. These are most abundant. Cream to white color, and burn light buff to white. Very fine grained, plastic, good bonding strength, and deformation temperature of cone 33 to 35. With grog they mold readily, dry and burn safely. Used as paper and rubber fillers as well as for ceramic purposes. Some of the lenses cover more than 650 acres, and the thickness ranges from 10 to 40 feet, with a known maximum of 52 feet.

5. Bauxitic clays. These have a $SiO_2 : Al_2 : O_3$ ratio of 1.8 : 0.8, but as this decreases the ease of slacking, plasticity and dry strength decrease. An oolitic or pisolitic structure may be present. The hardness is variable and refractoriness cone 35 to 38. They may be associated with bauxites or white clays and are well adapted to manufacture of refractories.

6. Bauxite. The alumina content ranges from 52 to 61, and the material may grade into bauxitic clay. The refractoriness is cone 37 to 40. The flint-clays and hard clays are well differentiated but all gradations may be found between hard and soft clays.

Most of the clays are now being mined in Wilkinson and Twiggs counties, although there are also important developments in Taylor, Glascock and Richmond counties.

It is probable that over 80 per cent of the white clay mined in both Wilkinson and Twiggs counties is washed.

There seems little doubt that the Cretaceous belt of Georgia contains extensive deposits of valuable clays, which will be widely used when a more uniform product is developed, and further experiments demonstrate their usefulness for different purposes.

PHYSICAL TESTS OF GEORGIA CRETACEOUS CLAYS

Clay	Crude			Cone 01				Cone 11			
	Water of plasticity	Volume shrinkage	Drying behavior	Volume shrinkage	Porosity	Burning behavior	Color No.	Volume shrinkage	Porosity	Color No.	Deformation cone
G. 1	41.06	24.83	good	20.54	35.75	good	3	40.05	29.20	8	34
G. 2	31.76	11.56	poor	13.83	50.71	poor	1	25.40	41.25	2	34
G. 5	38.50	22.68	good	13.01	41.37	good	2	38.01	22.82	3	34½
G. 6	44.50	24.97	fair	14.34	43.47	poor	2	47.27	12.65	3	34
G. 8	42.33	28.19	good	14.46	40.14	good	3	35.59	16.37	6	34
G. 18	28.96	14.21	poor	16.96	50.20	poor	7	55.32	24.00	10	34

All tests from U. S. Bur. Mines, Bull. 252. Of the color numbers, No. 1 represents the best or whitest, and No. 10 the poorest, a decided brown. For explanation of sample numbers see next table.

CHEMICAL ANALYSES OF GEORGIA CRETACEOUS CLAYS

	Moist. 105° C.	Ignition loss	SiO_2	Al_2O_3	Fe_2O_3	TiO_2	P_2O_5	CaO	MgO	K_2O	Na_2O	S
G. 1 Crude	2.05	12.67	45.61	36.15	1.47	0.77	0.05	0.80	0.30	0.43	0.00	0.02
G. 1 Washed	2.19	12.83	45.76	36.04	1.44	1.36	.06	.15	.36	.19	.00	.02
G. 2 Crude	.59	19.62	31.79	45.46	.66	1.68	.07	.11	.17	.00	.00	.04
G 2. Washed	.46	19.09	32.35	46.06	.54	1.40	.04	.14	.02	.00	.11	.04
G. 5 Crude	.98	12.73	45.78	37.01	1.11	1.32	.06	.35	.18	.75	.03	.06
G. 6 Crude	1.09	13.27	45.74	37.05	1.41	1.32	.08	.15	.10	.00	04	.05
G. 8 Crude	1.33	12.40	47.67	35.52	1.26	1.28	.04	.25	.37	.16	.04	.08
G. 18 Crude	.86	23.19	18.10	47.85	7.60	2.08	.05	.26	.29	.00	.00	.02
G. 14 Crude	.46	25.41	14.42	56.23	.96	2.34	.01	.31	.12	.00	.00	.06

All from U. S. Bur. Mines, Bull. 252.

1. Hard clay; 2. Bauxite clay; 5. Soft clay; 6. Semi-hard clay; 8. Semi-hard clay; 18. Low grade bauxite high in iron; 14. Good grade bauxite.

Clay-working industry.—In 1925 Georgia is said to have produced 41 per cent of all the white clay mined in the United States. The clay products include common brick, face-brick, hollow building tile, sewer-pipe, flue-lining, wall-coping, red earthenware, fire-brick, architectural terra-cotta, etc.

REFERENCES ON GEORGIA CLAYS

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See also forthcoming report of Ga. Geol. Survey.

ILLINOIS

The clay- or shale-bearing formations of this State are the Ordovician, Devonian, Mississippian, Pennsylvanian, Cretaceous, Tertiary, and Pleistocene.

Ordovician

So far as known this is of little importance, but the Cincinnati shale outcropping in Daviess and Boone counties, may prove of value for the manufacture of brick, hollow brick, and perhaps earthenware, since the same material has been successfully used in Iowa.

Devonian

This formation in Illinois contains shales but they have not been utilized.

Mississippian

The rocks of this age in Illinois are mostly limestones and sandstones, but a few shale deposits occur, and these have been worked at one locality.

PENNSYLVANIAN

The Pennsylvanian formations underlie a large part of the State (Fig. 111). They consist of a series of coal beds, shales, sandstones and clays, those underlying the coal being sometimes of a refractory character.

The Pennsylvanian shales are worked at several localities for paving-brick, and structural clay products. There is usually an overburden of loess or glacial deposits and sometimes weathered shale.

The refractory clays occur at the base of the Pennsylvanian, and outcrop along its border in the western part of the State. This fire-clay, which is regarded by some as the equivalent of the Cheltenham fire-clay of Missouri, extends from Rock Island County, south through Madison County, and is below the horizon of Coal No. 1 or No. 2, but in places the coal may be absent. South of Madison County the clay is not refractory. This clay is reported to be used in the manufacture of fire-brick, paving-brick, sewer-pipe and locally for stoneware, as in Greene County. Fire-clay is dug at Alsey, Scott County, in MacDonough County, and at several localities in La Salle County. In Grundy County there is a deposit of flint-clay in the coal measures, which is at least 30 feet thick.

CRETACEOUS

The Ripley formation extends northward from Tennessee, and forms a curved belt in southern Illinois, varying from five to fifteen miles in width. Clays and sands are present, the former being worked for stoneware (Ref. 4).

TERTIARY

The Midway formation which is exposed in bluffs along the Ohio River carries fullers' earth but no plastic clays of value (Ref. 4).

In northwestern Union County there occur a group of basin-like deposits of Tertiary age, which contain an interesting series of clays that have been worked especially near Mountain Glen. The clays are white, to bluish white and pink, and highly plastic. They appear to be underlain by sand and overlain by sand and gravel. Small quantities of lignite are found in the bluish-white clay. Some of the deposits are 30 to 50 feet thick but they appear to be of small areal extent. The type clay has high plasticity and drying shrinkage, with medium to low bonding strength, firing to a white to cream-colored body, and fusing at about cone 33.

The clays have been used for bond clays in the manufacture of crucibles, abrasive wheels and miscellaneous refractories (Ref. 4, 7).

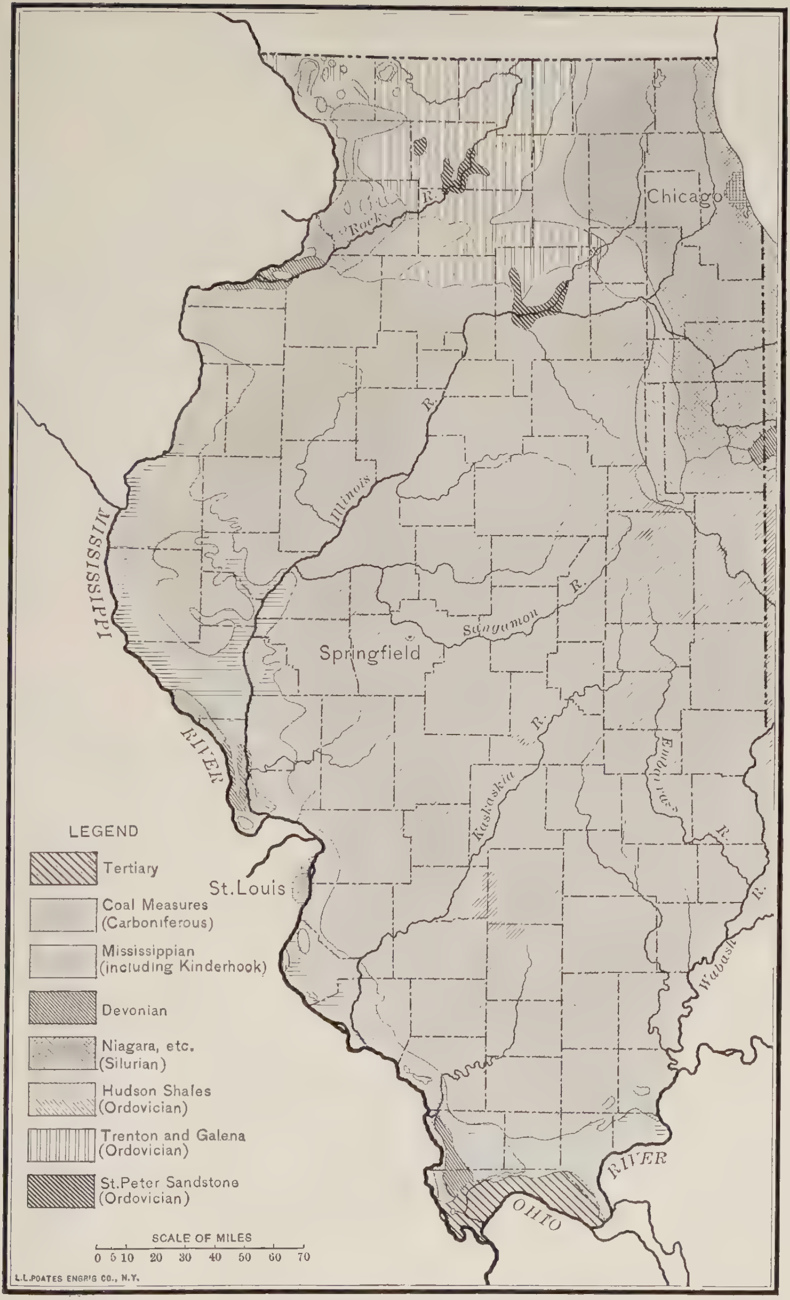

FIG. 111.—Map of Illinois, showing distribution of geologic formations. (After Ill. Geol. Surv., Bull. 4, 1907.)

PLEISTOCENE

This forms a most abundant source of brick- and tile-clays in many parts of the State. Around Chicago these clays occur as lake deposits

ANALYSES OF ILLINOIS FIRE-CLAYS

	I	II	III	IV	V	VI	VII	VIII
Silica (SiO_2)	71.58	64.88	65.14	55.96	54.80	56.28	68.12	58.06
Alumina (Al_2O_3)	18.31	21.54	21.53	29.47	29.44	26.68	20.08	26.57
Ferric oxide (Fe_2O_3)	1.51	1.86	1.59	1.57	1.70	3.24	1.76	1.23
Titanium oxide (TiO_2)	1.40	1.26	1.60	1.60	0.82	1.28	1.16	0.14
Volatile	5.27	6.83	7.37	8.25	8.84	10.28	6.31	9.84
Moisture	1.41	2.58	1.62	1.41	2.37	1.74	1.19	4.62
Total	99.48	98.95	98.85	98.26	97.97	99.50	98.62	100.46
Cone of fusion	28	28	29	31 ?	30+	22+	30	29+
Burned at 1120° C.	Porous buff	Hard buff	Porous lt. buff	Porous lt. buff	....	....	....	....

I. Potter's clay, Round Knob, Massac County.
II. W. Kortie farm, Massac County. Ripley formation.
III. IV. } Clays from near Monmouth, used in stoneware manufacture. Coal measures.
V. Utica Fire Brick Co., Utica, La Salle County. Coal measures.
VI. Pioneer Fire Proofing Co., Ottawa, La Salle County. Coal measures.
VII. Drake, Green County. Coal measures.
VIII. Clay from fault fissure between St. Louis limestone and Mansfield sandstones.
I–VIII. Bull. 4, Ill. State Geol. Surv., 1907.

PHYSICAL TESTS OF SOME ILLINOIS CLAYS

	I	II	III	IV	V	VI
Water of plasticity, per cent	37.4	23	22	25.6	18	14.9
Modulus of rupture, pounds per square inch	142	380	328	497	59.6	103*
Linear air shrinkage, per cent	5.6	5.0	6.0	9.3	3.6	1.5
Porosity at cone 9	3.2	2.0	10.0	8.2	17.0	......
Linear shrinkage at cone 9	11.5	6.0	6.0	5.1	5.0	2.2
Color at cone 9	gray	gray	cream	cream	......	......
Cone of fusion	33	26	28	28	28	......

* Tensile strength.

I. Refractory clay, Union County.
II. Stoneware clay, Greene County.
III. Fire brick clay, Scott County.
IV. Fire brick clay, La Salle County.
V. Flint clay, Grundy County.
VI. Paving brick clay, Alton.
I–V, Jour. Amer. Cer. Soc., Vol. v, p. 685, 1922. VI, Ill. Geol. Surv., Bull. 9.

of considerable extent, but they are highly calcareous and often pebbly. In other parts of the State the material used may be loess, boulder clay, or alluvial deposits bordering rivers.

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INDIANA

The Ordovician, Silurian, Devonian, and Carboniferous contain extensive shale-deposits, but only the last have thus far proven of commercial value.

ORDOVICIAN

The Ordovician rocks outcrop only in the southeast corner of the State, and these are often covered by a thin drift layer. The only shales are the Hudson River, but these are too calcareous to use, and of no value even when weathered.

SILURIAN

The beds of this age underlie a large area in eastern and north central Indiana, but carry few shales, and these are of no value.

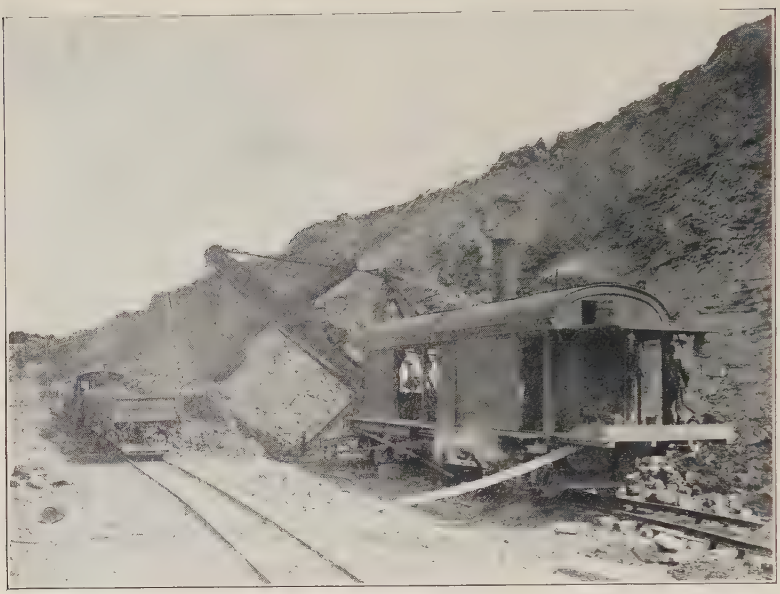

Fig. 112.—Carboniferous shale used for paving-brick. Galesburg, Ill. The excavating is done with a steam-shovel. (Photo loaned by Ill. Geol. Surv.)

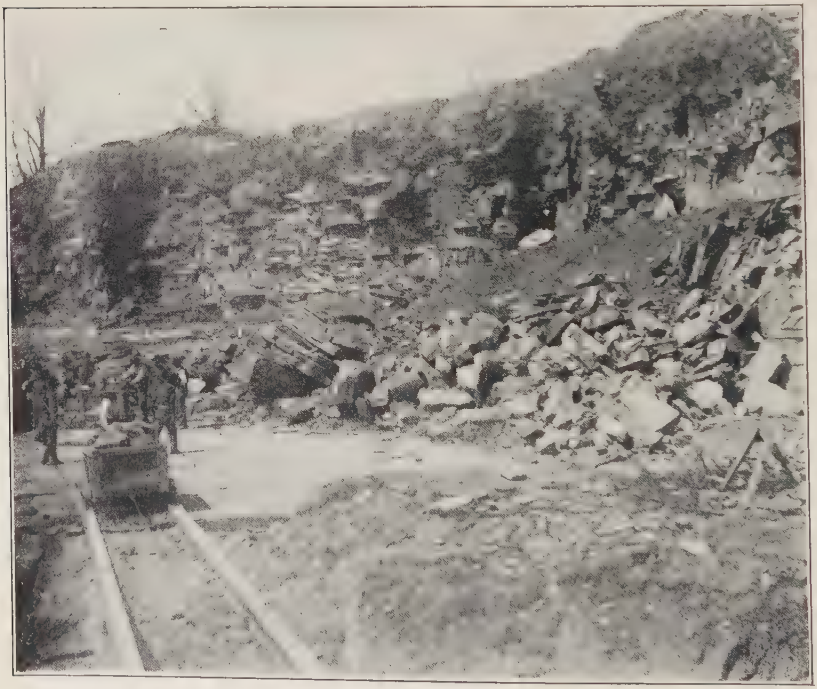

Fig. 113.—View in Knobstone shale-pit, Crawfordsville, Ind. (After Blatchley, Ind. Dept. Geol. and Nat. Res., 29th Ann. Rept., 1895.)

DEVONIAN

The Devonian beds underlie a great area, extending northwest and southeast through central part of State, but offer little promise to the clay-worker, as they are usually too bituminous.

MISSISSIPPIAN OR LOWER CARBONIFEROUS

The rocks of this age afford residual clays and shales.

Residual clays.—Since a large part of the Mississippian area occurs in the driftless region, the residual clays derived from underlying limestone and sandstones are available, and occur at many points in Monroe, Lawrence, Orange, Harrison, and Floyd counties, as well as parts of the adjoining ones, so that they form the most important source of the brick- and tile-clays worked in these counties.

Shales.—Those of the Knobstone formation (Fig. 114) are important and destined to become prominent in the future, although they have been neglected in the past. Indeed they are next to the coal-measure shales, the most important in the State. According to Blatchley (Ref. 3) the Knobstone shale forms the surface-rock of a strip of territory 3 to 38 miles wide on the eastern side of the Lower Carboniferous area, extending from the Ohio River southwest of New Albany in a west of north direction to a point a few miles south of Rensselaer, Jasper County.

While the formation is often covered by a heavy mantle of drift, many excellent exposures have been formed by the cutting of the larger streams, as along the West White River near Martinsville; along Sugar Creek, above and below Crawfordville, and along Shawnee Creek south of Attica. Many additional outcrops have been found in other counties within the belt occupied by these shales.

The Knobstone formation consists of blue-gray shales, shaly sandstones, and sandstones, with rarely a little limestone. Nodules of siderite are not uncommon.

These shales are utilized at New Albany for stiff-mud and dry-press brick; it is also possible that they could be used for sewer-pipe when admixed with some of the Carboniferous under-clays.

Among the Chester shales, those belonging to the Sample, Elwren, Indian Springs, and other divisions of the Chester group, have been used for ceramic purposes (Ref. 5). They vary in quality and quantity.

CARBONIFEROUS

The rocks of this period carry the most valuable clay-deposits of the State, and cover an area of about 7500 square miles in fourteen counties of western and southwestern Indiana (Fig. 114).

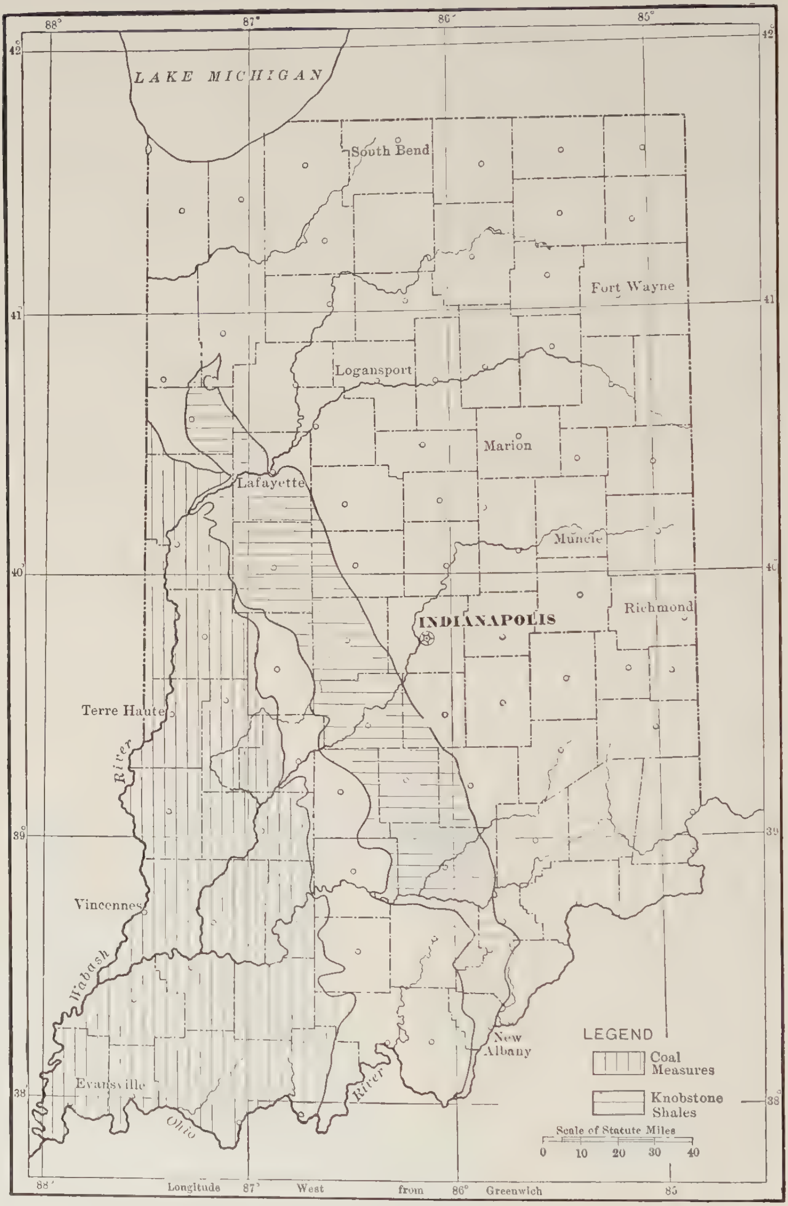

FIG. 114.—Map. of Indiana, showing areal distribution of coal-measure shales and Knobstone shales. (Adapted from map compiled by Hopkins.)

They form part of a large basin, underlying western and southwestern Indiana and southern Illinois, so that those in Indiana are on the eastern edge, and therefore dip southwestward and westward. This being so, the lowest rocks of the section outcrop on the eastern and northeastern edge of the area, while the higher lying ones outcrop farther westward.

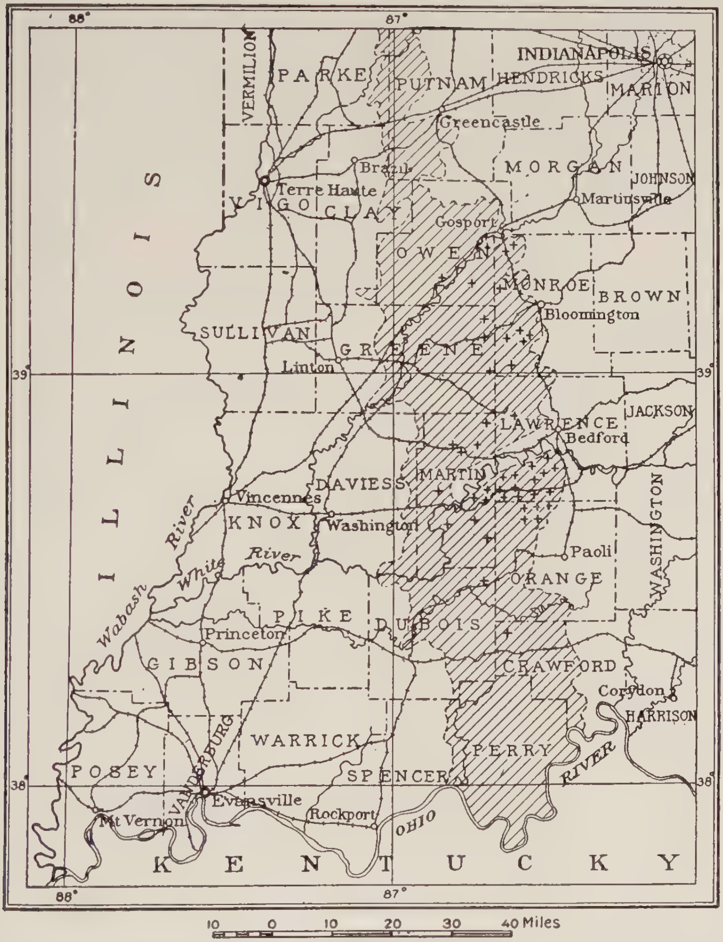

Fig. 115.—Map of part of Indiana showing area (shaded) that may contain indianaite. +, known outcrop. (U. S. G. S., Bull. 708.)

The Carboniferous rocks consist of a lower member, the Mansfield sandstone, and an upper member, the coal-measures.

Indianaite.—At the base of the Mansfield sandstone near its contact with the Chester shales of the Mississippian, which underlie it unconformably, there is a deposit of white clay which was called Indianaite by Cox in 1874 [3] and has also been referred to as kaolin, halloysite, and allophane. The best-known deposit is at Huron, Lawrence County, but it has been found in a number of other localities (Fig. 115). The material whose thickness is variable, from perhaps 4 to 11 feet, is at times massive, waxy and lustrous, at others earthy, and may also contain druses lined with a hyaline mineral. Some of the waxy variety shows a blue color when moist, but which fades out on drying. Iron and manganese stains are occasionally present, and on the outcrop the clay usually shows a mahogany color.

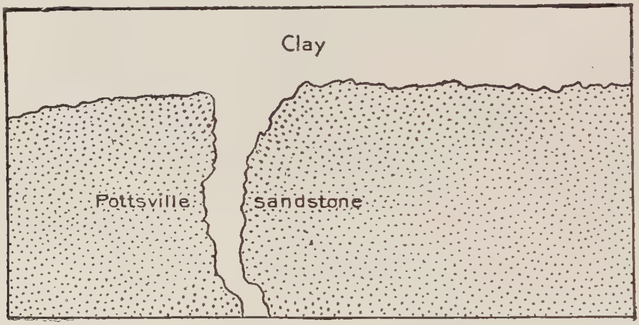

Fig. 116.—Indianaite overlying sandstone and vein of indianaite extending into the sandstone in Gardner mine, near Huron, Ind. (After Logan, U. S. Geol. Surv., Bull. 708.)

Scattered through the clay are angular fragments of Mansfield sandstone, and in some instances bands of the clay traverse the sandstone at right angles to the bedding (Fig. 116), or even permeate it in indefinite streaks.

Under the microscope the waxy clay shows large flakes of isotropic material, and numerous spherulite-like grains, which exhibit the interference colors of kaolinite. Rutile in very minute grains is abundant. The earthy variety shows radiating bunches and spherulites of a hydromica, possibly sericite, and also kaolinite. The hyaline material referred to above has a composition closely resembling schroetterite.

There has been much discussion regarding the origin of this kaolin, and while several theories have been advanced to explain its origin, all acknowledge its residual character, and that of the inclosing rocks, as sedimentary.

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[1] Cox, E. T., Porcelain, tile and potters clays, Ind. Geol. Surv., 8th, 9th and 10th Ann. Repts.

E. T. Cox[1] argued that the kaolin occupied the position of a limestone bed, and that carbonated waters, acting on the latter, replaced the limestone with kaolinite. Thompson[2] seconded this theory, but added the belief that the surface-water had leached the alumina and silica from the overlying sandstones.

Lesquereaux, on the other hand, believed that the kaolin was formed by the burning-out of coal-beds, a view in which Ashley concurred.

It seems to the author that there are certain marked objections to the latter theory. The burning-out of the coal would probably produce sufficient heat to cause some dehydration of the kaolin, whereas there is no evidence of this. In just what way the kaolin resembles baked fire-clay is not mentioned.

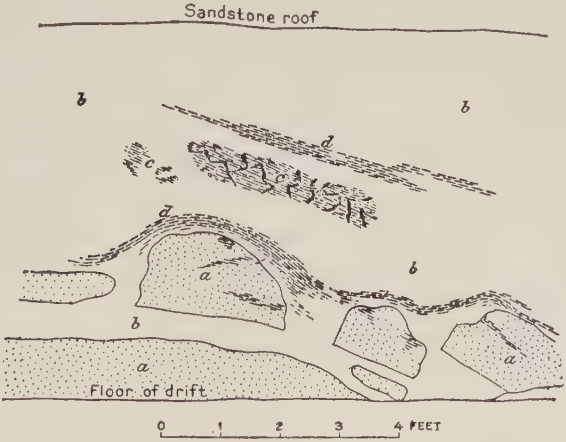

Fig. 117.—Section along north side of second cross entry on east side of tunnel, in Gardner mine, near Huron, Ind. *a*. Sandstone; *b*. milk-white clay; *c*. waxy clay; *d*. clay that shows banded structure. (From sketch made by author.)

It is not necessary to suppose any complex chemical reactions in order to derive kaolin from limestone. A calcareous rock, containing aluminous matter very low in impurities, might easily yield a mass of kaolin by simple leaching, and residual limestone clays of rather high purity are known in Missouri and also Virginia.

More recently Logan has suggested that the clay is the result of replacement of the quartz pebbles of the Mansfield sandstone by aluminum sulphate, the latter being formed by bacterial action from the Chester shale (Ref. 4). The author is in thorough agreement with him so far as the replacement theory is concerned, but finds it difficult to accept the bacterial theory (Ref. 6).

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[1] Sixth Ann. Rept. Geol. Surv. of Ind., 1874, p. 15.

[2] Ind. Dept. Geol. and Nat. Hist., 15th Ann. Rept., p. 37, 1886.

Coal-measure clays and shales.—The Coal-measures include a series of coals, clays, shales, and sandstones (Fig. 118), and are found in a number of counties in the southwestern part of the State (Fig. 114).

Ashley [1] has divided them vertically into eight divisions designated by Roman numerals, these divisions being based on the position of some principal coal-beds or horizons, the type section occurring in Clay and Vigo counties. The Mansfield sandstone found in general along the eastern edge of the coal-field forms division I, and the main-worked coals, clays, and shales occur above it stratigraphically.

A part of a typical vertical section showing the arrangement of the different strata of the coal-measures and their relation to each other is given by Blatchley (Ref. 3) as follows:

		Feet	Inches
1.	Soil- and surface-clay	5	2
2.	Sandstone, massive or shelly	2	8
3.	Blue compact shale	27	0
4.	Coal VII	4	10
5.	Fire-clay	6	2
6.	Drab siliceous shale	18	0
7.	Limestone	3	8
8.	Black bituminous shale	2	4
9.	Coal VI*b*	0	8
10.	Fire-clay	5	6
11.	Sandstone	13	0
12.	Dark-grey shale	11	2
13.	Coal VI	6	3
14.	Hard impure bluish fire-clay	11	0
15.	Sandstone	21	0
16.	Blue limestone	11	0
17.	Black slaty bituminous shale	5	4
18.	Coal V	5	2
19.	Fire-clay	4	8

The fire-clays (Nos. 5, 10, 14, and 19) are almost universal accompaniments of the overlying coal-seams. They are usually 1 to 6 feet thick, and are a soft homogenous clay, whitish or gray in color, highly plastic, and often of excellent refractoriness. At times, however, these under-clays are composed of a hard, bluish, siliceous clay with more or less pyrite and other impurities.

No. 14 is of this character, and similar clays usually occur beneath coals III and V, but those below coals II, IV, VI, and VIII are often of excellent quality.

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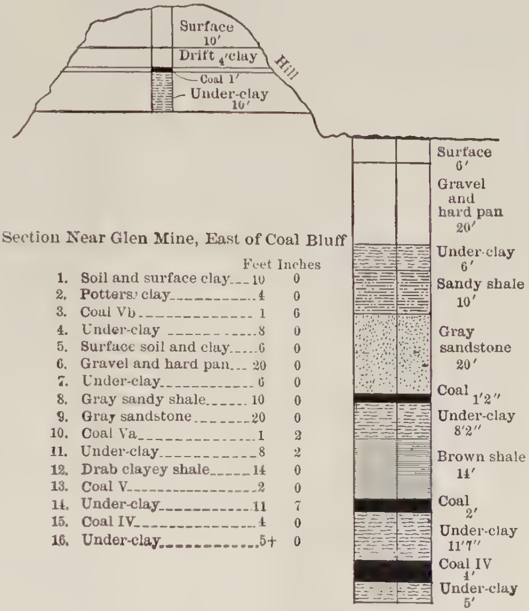
[1] Ind. Dept. Geol. and Nat. Res., 23d Ann. Rept., 1899.

The blue, gray, and drab shales (Nos. 3, 6, and 12) make up the greater part of the Coal-measure rocks of Indiana, and include the most valuable clay-deposits found in the State. When freshly exposed they are usually hard, but weather down easily to a plastic clay.

The relations of the shales, clays, and coal are such that the three can often be mined by one shaft.

The Coal-measure clays and shales are worked for a variety of purposes, including pressed- and paving-brick, fireproofing, sewer-pipe, stoneware and fire-brick.



Section Near Glen Mine, East of Coal Bluff

		Feet	Inches
1.	Soil and surface clay	10	0
2.	Potters' clay	4	0
3.	Coal Vb	1	6
4.	Under-clay	8	0
5.	Surface soil and clay	6	0
6.	Gravel and hard pan	20	0
7.	Under-clay	6	0
8.	Gray sandy shale	10	0
9.	Gray sandstone	20	0
10.	Coal Va	1	2
11.	Under-clay	8	2
12.	Drab clayey shale	14	0
13.	Coal V	2	0
14.	Under-clay	11	7
15.	Coal IV	4	0
16.	Under-clay	5+	0

FIG. 118.—Section near Glen Mine, Coal Bluff, Ind., showing association of coals, under-clays, etc. (After Blatchley, Ind. Dept. Geol. and Nat. Res., 29th Ann. Rept., p. 183, 1905.)

At Brazil, Clay County, which is a most important clay-working center, the following section is instructive:

		Feet	Inches
1.	Soil and yellow clay	12	0
2.	Bowlder clay, blue	7	0
3.	Gray clayey shale	33	0
4.	Coal V	2	3
5.	Under-clay (potters' clay)	3	2
6.	Blue clayey shale	19	0
7.	Bituminous fossil shale	1	6
8.	Coal IV	3	6
9.	Under-clay	5	4

No. 9 and an overlying shale are used for sewer-pipe, flue-linings, wall-coping, etc. No. 3 is also used for a variety of purposes.

Logan (Ref. 5) states that a large number of the thirty-five coal-beds found in the State have associated fire-clays. Those under the coals known as Upper Block, Minshall, III, III*a* and V, are used extensively for ceramic purposes.

Pleistocene Clays

These are soft, plastic clays, found at the surface or at no great distance below it, and, while occurring over a large part of the State, they are especially important in the northwestern part of Indiana, and on this account have been made the subject of a special report. (Ref. 1.)

In this region three clases are distinguishable, namely, drift-clays or "hard-pans," alluvial clays, and silty or marly clays.

The drift-clays are the most common type, forming a large percentage of the unstratified morainic material, but they are usually too impure and calcareous for making anything but common brick and tile.

The alluvial clays form larger deposits along the lowlands and second bottoms of the large streams of northwestern Indiana, having been formed during periods of overflow, and in some places showing a thickness of 30 to 90 feet.

The silty or marly clays resemble those of the preceding class very closely, but differ in having been deposited in bays, lakes, or harbors in quiet water. These clays are usually finer grained than the alluvial ones, thinly laminated, and often highly calcareous, so that they produce a buff product. They are an important source of brick and tile material in Benton, Newton, Jasper, Starke, Lake, Porter, Laporte, and St. Joseph counties.

In other parts of the State there are many scattered deposits of surface-clays used for brick and tile, while south of the terminal moraine in southwestern Indiana there are many deposits of loess which are available for the same purpose.

The analyses on pp. 427 and 428 are given by Blatchley (Ref. 3) as representative of the different types of Indiana clays and shales.

REFERENCES ON INDIANA CLAYS

1. Blatchley, W. S., Clays and Clay Industries of Northwestern Indiana, Rept. of Indiana State Geologist for 1897, p. 106.
2. Blatchley, W. S., Preliminary Report on the Clays and Clay Industries of the Coal-bearing Counties of Indiana, Ind. Dept. of Geol. and Nat. Res., 20th Ann. Rept., p. 23, 1896.
3. Blatchley, W. S., The Clays and Clay Industries of Indiana, Ind. Dept. Geol. and Nat. Res., 29th Ann. Rept., pp. 13–658, 1904.
4. Logan, W. N., For description and origin of Indianaite see, Ind. Acad. Sci., 1918, p. 177; Science, new ser., XLIX, p. 197, 1919; Dept. Conserv., Ind., Div. Geol., Pub. No. 6, 1919; U. S. Geol. Surv., Bull. 708, p. 147, 1922.
5. Logan, W. N., Refractory Clays and Shales of Indiana, Jour. Amer. Ceram. Soc., Vol. VII, p. 201, 1924.
6. Ries, H., U. S. Geol. Surv., Bull. 708, p. 154, 1922.

Analyses of Indiana Clays

	I	II	III	IV	V	VI
Silica (SiO_2)	59.77	58.83	65.78	67.65	55.09	83.44
Alumina (Al_2O_3)	20.60	22.84	14.79	19.97	20.76	10.36
Ferric oxide (Fe_2O_3)	2.22	5.13	8.03	0.72	3.00	0.27
Ferrous oxide (FeO)	3.70	1.44	....	....	4.01	0.28
Lime (CaO)	0.64	0.49	0.54	0.48	1.51	0.36
Magnesia (MgO)	1.98	1.56	1.42	0.59	1.18	0.14
Potash (K_2O)	3.10	4.18	2.82	1.75	2.36	0.03
Soda (Na_2O)	0.85	0.63	0.97	2.29	0.34	0.71
Titanic acid (TiO_2)	0.80	0.70	1.00	1.01	1.20	1.29
Carbon dioxide (CO_2), etc.	0.90	....	0.26	3.04	....	....
Water (H_2O)	4.53	5.22	4.98	5.96	7.01	3.15

	VII	VIII	IX	X	XI	XII
Silica (SiO_2)	69.23	65.25	59.64	63.88	70.60	66.11
Alumina (Al_2O_3)	18.97	17.30	19.14	17.85	13.89	13.78
Ferric oxide (Fe_2O_3)	1.57	2.30	3.39	5.38	2.83	5.35
Ferrous oxide (FeO)	0.55	....	4.20	....	3.56	....
Lime (CaO)	0.12	0.50	0.26	0.38	0.60	1.67
Magnesia (MgO)	0.36	0.20	2.31	1.47	0.50	1.78
Potash (K_2O)	2.27	1.56	3.53	3.98	2.76	2.11
Soda (Na_2O)	0.33	0.98	0.80	1.29	1.60	1.15
Titanic acid (TiO_2)	1.50	....	1.05	0.91	0.43	....
Carbon dioxide (CO_2), etc.	....	6.50	0.35	....	0.51	....
Water (H_2O)	5.46	5.40	4.36	4.99	3.19	6.34

	XIII	XIV	XV	XVI	XVII
Silica (SiO_2)	71.20	72.56	50.56	50.47	44.75
Alumina (Al_2O_3)	18.56	10.44	13.11	12.77	38.69
Ferric oxide (Fe_2O_3)	1.34	7.45	2.98	2.44	0.95
Ferrous oxide (FeO)	0.15	0.43	2.32	2.52	....
Lime (CaO)	0.14	0.82	7.87	8.17	0.37
Magnesia (MgO)	0.52	1.09	5.06	5.22	0.30
Potash (K_2O)	0.32	2.05	3.74	3.70	0.12
Soda (Na_2O)	1.26	0.73	0.70	0.73	0.23
Titanic acid (TiO_2)	0.88	0.31	1.00	1.45	....
Carbon dioxide (CO_2), etc.	....	....	9.62	9.80	....
Water (H_2O)	6.30	4.54	2.76	3.14	15.17

RATIONAL ANALYSES OF THE PRECEDING

	I	II	III	IV	V
Quartz	26.04	22.81	34.34	28.29	20.90
Feldspathic detritus	8.37	8.30	12.58	34.77	2.03
Ferrous carbonate	2.37	....	....	....	6.46
Magnesium carbonate	....	....	0.50	....	1.13
Clay substance	63.22	58.89	52.58	36.94	69.48

	VI	VII	IX	X	XI
Quartz	46.33	39.36	25.57	17.93	56.65
Feldspathic detritus	39.28	1.67	6.86	42.03	16.63
Ferrous carbonate	....	....	....	....	1.07
Magnesium carbonate	....	....	0.67	....	0.08
Clay substance	14.39	58.37	66.90	40.04	25.57

LOCALITIES OF THE PRECEDING

No.	Location	Geological Age
I	Mecca, Mecca Coal and Mining Company	Carboniferous shale
II	Mecca, Mecca Coal and Mining Company	
III	Cayuga, Cayuga Brick and Coal Company	
IV	Mecca, Mecca Coal and Mining Company	Coal-measures under-clay
V	Cayuga, Cayuga Brick and Coal Company	
VI	W. Montezuma, Burns & Hancock	
VII	Huntingburg, Bockting Bros	
VIII	Huntingburg, C. Fuchs	
IX	Blue Lick	Knobstone shale
X	New Albany	
XI	Martinsville, Branch & Sons	
XII	Terre Haute	Alluvial
XIII	Princeton	Surface Loess
XIV	Four miles south of Bloomington	Residual
XV	Hobart	Pleistocene
XVI	Michigan	
XVII	Indianaite, Huron, Dr. Gardner	Residual

IOWA

Every great rock formation of Iowa, except one, the Sioux quartzite contains more or less important clay- or shale-deposits, but the different ones represent a wide range of structural characters and physical or chemical properties, these variations occurring sometimes within the same formation.

Iowa does not possess any strictly first grade refractory clays in commercial quantities. Those of the underclay type seldom reach cone 25 fusion-point, and the more refractory ones lack in plasticity. Lack of uniformity in thickness and constitution is another drawback. The few deposits meriting attention are certain Pennsylvanian clays in Henry and Lee counties of southeastern Iowa, the gritty Carboniferous under-clays of Boone and Webster counties, and the white Niagara clays of Jackson and Clinton counties.

CAMBRIAN

Saint Croix sandstone.—This carries a few shale-beds which outcrop in portions of Allamakee and Clayton counties, but nothing is known regarding their economic value.

ORDOVICIAN

Galena-Trenton.—Although essentially a limestone formation, this nevertheless contains a few beds of shale, which may be adaptable to pottery manufacture. The best exposure is on Silver Creek, Makee township, Allamakee County. Concretions and fossils are apt to render this shale worthless.

Maquoketa shale.—This, the oldest shale formation of importance in the State, forms a narrow, sinuous band from Jackson County on the south to Winneshiek and Howard counties. The shale is divisible into two groups, the upper consisting of a plastic clay, with occasional limestone layers, while the lower is of lean fissile shales, with some earthy, fossiliferous beds. They are mostly red-burning, but may at times be quite calcareous, and though their chief use is for common brick, they have also given excellent results for earthenware manufacture and hollow brick.

SILURIAN

The beds of this system are practically devoid of shale-deposits.

DEVONIAN

The lower argillaceous beds, known as the Independence formation, outcrop in limited measure in Cedar, Linn, and Buchanan counties, but are of no economic importance.

The upper shales, which are typically developed along Lime Creek

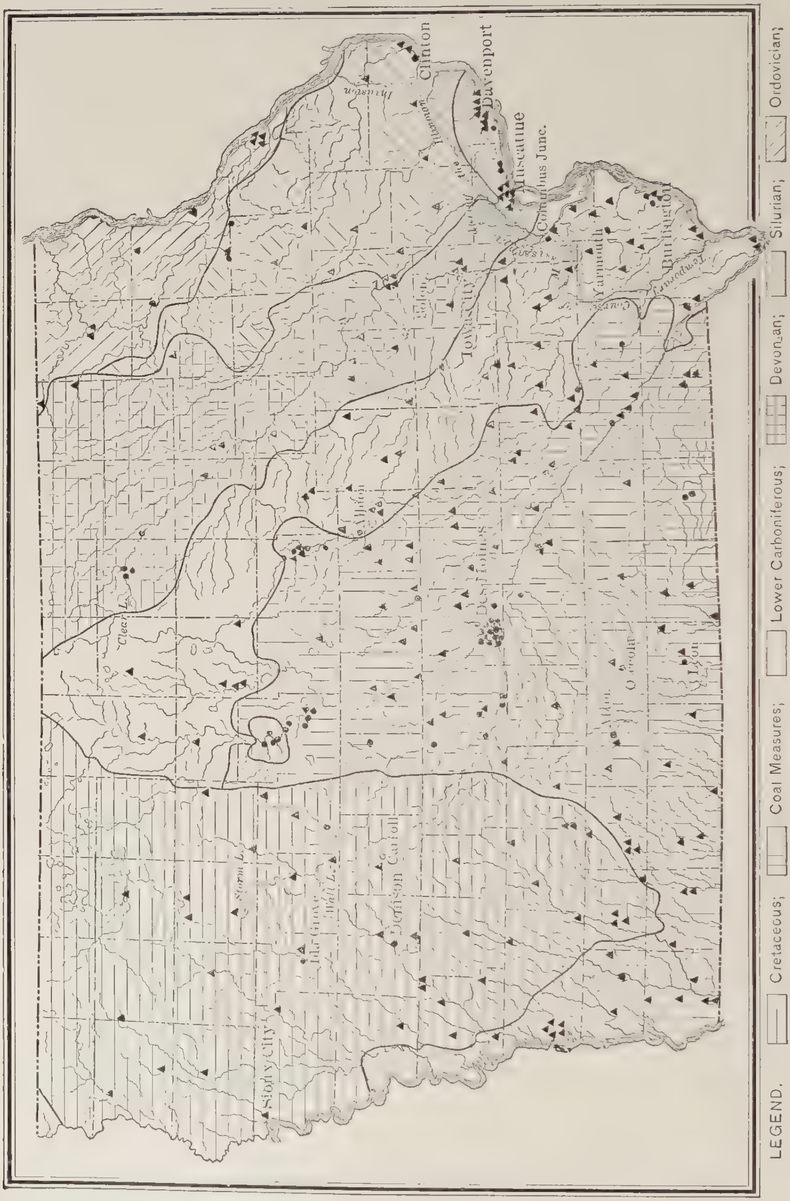


FIG. 119.—Map of Iowa, showing distribution of clay-bearing formations and location of clay and shale-pits. (After Beyer and Williams, Ia. Geol. Surv., XIV, 1904.)

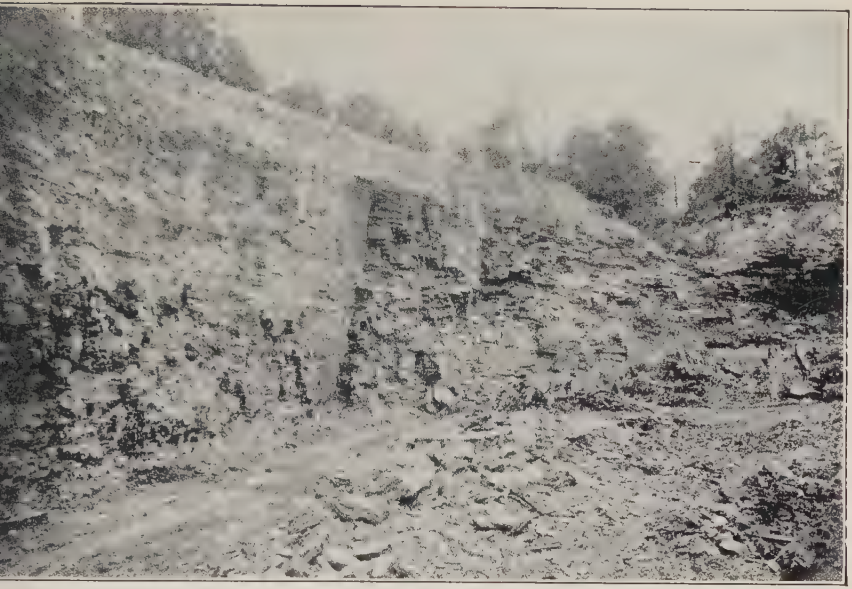


FIG. 120.—Carboniferous shale for paving-blocks near Veedersburg, Ind. (After Blatchley, 29th Ann. Rep., Ind. Dept. Geol. and Nat. Res., p. 80.)

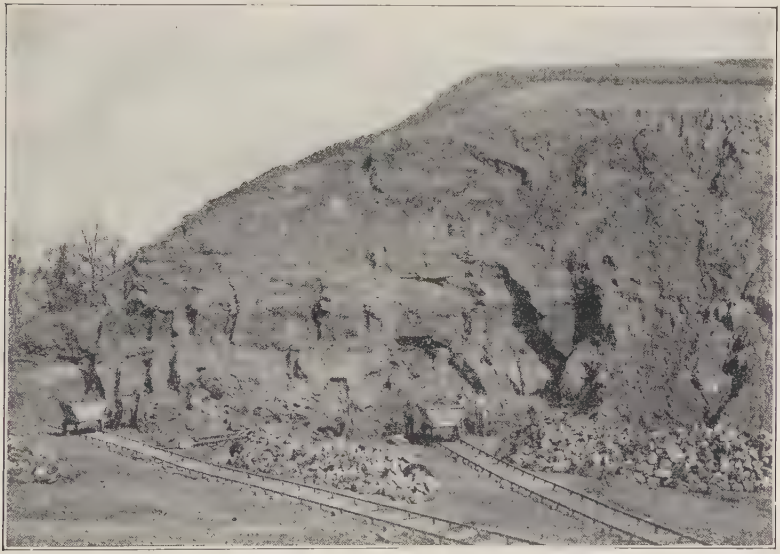


FIG. 121.—Cretaceous shale, Sioux City, Ia. (After Williams, Ia. Geol. Surv., XIV, p. 518, 1904.)

in Cerro Gordo and Floyd counties, and at Rockford and Mason City are of much greater value. Owing to a variable lime-content the clays burn either light red or cream, but in either case have yielded good results in the manufacture of common and hollow brick and drain-tile. The shales are too fusible to take a salt-glaze.

CARBONIFEROUS

Practically all of the great formations of the Carboniferous contain clays of importance, but those of the Kinderhook and Coal-measures are especially important. According to Beyer and Williams, " Rocks referable to the Carboniferous comprise the indurated rocks over nearly one-half of the surface of the State. The system may be divided into two parts: (1) the Lower Carboniferous beds, which are prevailingly calcareous in character, and (2) the Upper Carboniferous, in which arenaceous and argillaceous deposits predominate, with important limestone bands in the upper portion. The latter division contains all of the workable coal in the State. On account of the abundance of raw material suitable for the manufacture of clay wares and cheap fuel, the Upper Carboniferous or Coal-measures constitute the most important formation to the clay-worker in the State.

" The Lower Carboniferous comprises a belt averaging from thirty to forty miles in width, and extending diagonally across the State from Kossuth and Winnebago counties on the north to Des Moines and Lee counties on the south. Narrow strips have been laid bare by the lower courses of the Skunk and Des Moines rivers, and unimportant detached areas appear in Story and Webster counties. Three stages represent the Lower Carboniferous in Iowa, namely, the Kinderhook, Augusta, and Saint Louis."

Kinderhook.—The shales of this formation are specially prominent in Des Moines and Lee counties; they are red- or brown-burning and used for common brick.

Augusta.—These shales are of little importance except in Lee County, and even there are rather calcareous.

COAL-MEASURES

The rocks of this age cover nearly one-third of the State and carry a great range of argillaceous beds grouped as (1) argillaceous, (2) arenaceous, (3) carbonaceous or bituminous, and (4) calcareous varieties. These grade into each other both vertically and horizontally. Although the coal-measures are present in ninety-nine counties of the State, the clay-shales are utilized for making clay-products in but sixteen. The argillaceous shales are often found underlying the coal-seams, and are not uncommonly of refractory character, but the calcareous ones contain too much limey matter to be of great value. Those beds of the Coal-measures prominent along the Des Moines River contain argillaceous, bituminous, and arenaceous shales, while in the beds most prominent along the Missouri River the calcareous members are more prominent.

It is difficult to generalize regarding the clays of this series, but at any one point it is not uncommon to find several grades of clay ranging from common brick-clay to fire-clay in the same section. The shales are worked at a number of points, among which Van Meter, Dallas County; Des Moines, Polk County; Ottumwa, Wapello County; and Fort Dodge, Wapello County, may be mentioned. The clays are worked either as open pits or underground mining and the products include common and pressed-brick, paving-brick, hollow blocks, drain-tile, stoneware, and fire-bricks. Analyses of these are given on a later page.

CRETACEOUS

The Cretaceous of Iowa consists of a lower sandstone and shale series, the Dakota, and an upper series of interbedded sandstones, shales, and marly limestones. These rocks cover approximately the northwestern third of the State, shale-beds of this age being known in Sioux (Fig. 121), Plymouth, Woodbury, Sac, Calhoun, and Montgomery counties.

The shales show about the same textural and chemical range as the Carboniferous ones, but on the whole are more siliceous.

At Red Oak, Montgomery County, both white stoneware and fire-brick are made, and it has been suggested that washing might render the clay available for glass-pot manufacture. Other products from these shales are paving and common brick.

PLEISTOCENE

Covering all of the State, with the exception of a small area in the northeastern corner, is a thick mantle of glacial deposits which range in thickness from zero up to three or four hundred feet. The glacial drift is composed of a heterogeneous mass of bowlder beds, gravel, and sand-deposits, and more rarely beds of clay, which, owing to a natural washing process which they have undergone, are sufficiently plastic to be molded into clay wares. They often suffer, however, from the presence of lime pebbles or stones, and even if free from these are still unsatisfactory because of their high shrinkage, which causes a loss due to check-

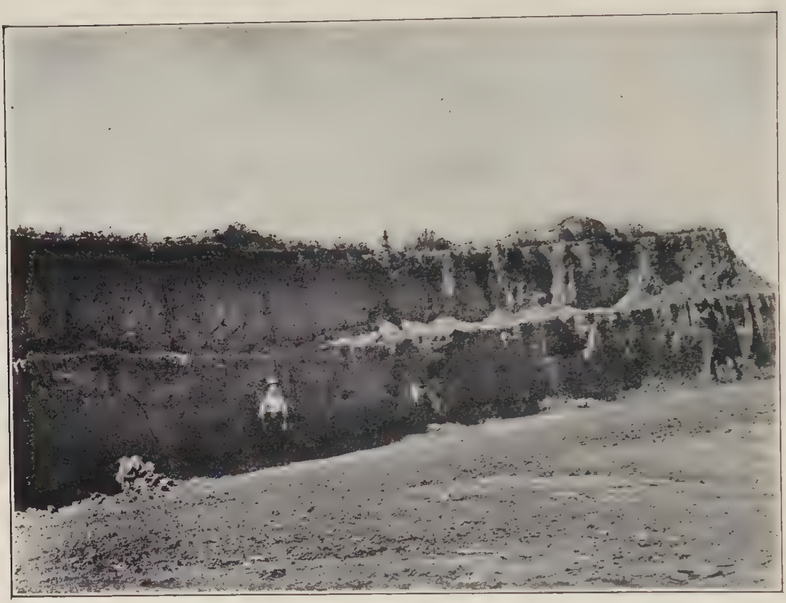


FIG. 122.—Loess-bank, Muscatine, Ia. (After Williams, Ia. Geol. Surv., XIV, 1904.)

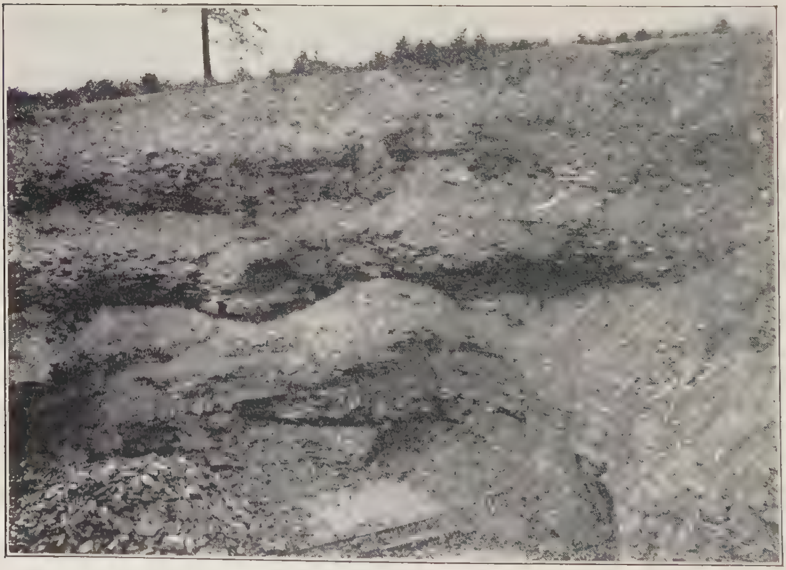


FIG. 123.—Bank of (Devonian) shale used for paving-brick, Cumberland, Md. (After H. Ries, Md. Geol. Surv., IV, p. 454, 1902.)

ing in drying and burning. A few of the drift-sheets, however, contain clays of satisfactory character for brick manufacture.

Loess.—Associated with the drift-sheets and of far greater economic importance are the massive structureless deposits of loess. (Fig. 122.) These consist of clays or clayey silts, which form a mantle over about two-thirds of the area of the State, affording an inexhaustible supply of brick material.

This occurs beyond the borders of the drift-sheets and even overlapping them. It covers more than one-half the surface of the State and shows great irregularity in thickness, being over one hundred feet thick along the Missouri River. It affords an exhaustless supply of material suitable for the manufacture of brick by the soft-mud, stiff-mud, or dry-press process, and moreover is a very cheap clay to work.

Of the several types of loess recognized in the State, the "gumbo" is noteworthy. This is a thoroughly oxidized and leached red clay which on drying breaks up into a number of angular fragments. In the southern part of the State the gumbo is gray or drab in color. Its peculiarity is its excessive shrinkage which precludes its use for the manufacture of brick, but makes it admirably adapted to the manufacture of burned-clay ballast.

The chemical composition of a number of representative Iowa clays and shales is given in the table on pp. 435 and 436.

ANALYSES OF IOWA CLAYS

ULTIMATE ANALYSES

	I	II	III	IV	V	VI	VII	VIII
Silica (SiO_2)	67.50	61.59	73.43	63.78	58.56	75.85	58.05	77.39
Alumina (Al_2O_3)	15.75	21.01	11.94	19.78	22.33	10.73	23.05	5.16
Ferric oxide (Fe_2O_3)	4.80	4.79	3.83	5.75	2.87	1.43	3.83	2.40
Lime (CaO)	2.57	3.58	1.00	1.55	3.60	1.00	0.30	3.65
Magnesia (MgO)	1.57	2.16	0.86	1.22	1.44	0.49	2.04	3.13
Potash (K_2O)	0.95	0.52	0.05	0.54	0.29	0.24	0.90	1.44
Soda (Na_2O)	1.56	1.13	0.95	1.20	1.08	0.70	2.04	2.79
Comb. water (H_2O)	3.22	4.51	4.33	2.92	7.11	6.38	8.10	1.46
Carbon dioxide (CO_2)	with moist.	......	0.90	with moist.	with moist.	with moist.	......	......
Sulphur trioxide (SO_3)	with moist.	0.95	1.65	with moist.	with moist.	with moist.	0.86	1.44
Moisture	2.88	0.42	0.63	3.88	2.98	3.18	0.96	0.13

Analyses of Iowa Clays *(continued)*

ULTIMATE ANALYSES

	IX	X	XI	XII	XIII	XIV	XV	XVI
Silica (SiO_2)	58.33	47.40	28.82	66.44	51.95	44.39	68.22	67.92
Alumina (Al_2O_3)	15.54	22.20	10.37	12.64	18.34	13.72	10.21	11.76
Ferric oxide (Fe_2O_3)	3.84	12.40	3.76	4.00	7.56	7.80	2.87	6.72
Lime (CaO)	9.42	0.70	19.14	4.02	4.14	7.88	3.90	1.63
Magnesia (MgO)	3.03	1.10	5.40	1.80	3.26	6.05	3.16	1.18
Potash (K_2O)	1.19	3.10	5.38	1.14	1.43	1.56	0.58	1.87
Soda (Na_2O)	1.76	0.50	7.41	1.90	2.69	5.29	1.68	1.92
Comb. water (H_2O)	3.47	7.90	16.24	5.83	7.39	12.18	1.52	5.36
Carbon dioxide (CO_2)	2.02	......	......	......	......	......	5.86	......
Sulphur trioxide (SO_3)	1.10	2.40	3.01	......	2.76	......	1.45	......
Moisture	0.42	2.10	0.43	2.33	0.42	0.89	0.62	1.49

Localities of the Preceding

No.	Locality	Geological age	Uses
I	Flint Brick Co., Des Moines	Coal-measures	Paving- and building-brick
II	Iowa Brick Co., Des Moines	Coal-measures	Paving-brick, builders, and hollow ware, bottom
III	Iowa Brick Co., Des Moines	Coal-measures	Ditto, top
IV	Flint Brick Co., Des Moines	Coal-measures	Paving-brick; green-brick mixture
V	Capital City Brick Co., Des Moines	Coal-measures	Brick and tile
VI	J. Holman, Sargent's Bluff	Cretaceous	Common, face, paving-brick, sidewalk brick
VII	Corey Pr. Br. Co., Lehigh	Coal-measures	Pressed face brick and ornamentals
VIII	Granite Br. Co., Cascade	Kinderhook	Common and paving-brick
IX	Cream City B. & T. Co., Rockford	Devonian	Brick and tile
X	Boone Br. & T. Co., Boone	Coal-measures	Paving, hollow ware, common brick
XI	Clermont	Maquoketa	Brick and tile
XII	Storm Lake	Drift	Drain-tile
XIII	Mason City	Devonian	Brick and tile
XIV	Edgewood	Maquoketa	Brick and tile
XV	Council Bluffs	Loess (Mo.)	Soft-mud, stiff-mud, and pressed brick
XVI	Gladbrook	Inland Loess	Pressed brick

These analyses are all from Vol. XIV, Ia. Geol. Surv., and have been kindly selected as representative by Professor I. A. Williams.

REFERENCES ON IOWA CLAYS

1. Beecher, M. F., An Investigation of Iowa Fire-clays, Ia. State Coll. Agr. Mech. Arts, Eng. Exper. Sta., Bull. 40, 1915; also Trans. Amer. Ceram. Soc., Vol. XVII, p. 102, 1915.
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3. Galpin, S. L., The Geology of the More Refractory Clays and Shales of Iowa, Ia. Geol. Surv., XXXI, Ann. Repts. for 1923 and 1924, pp. 53–90, 1925.
4. Whitford, W. G., and Whittemore, O. J., Possibilities of Pottery Manufacture from Iowa Clays, Ia. St. Coll. Agric., Vol. XII, Bull. 58.

KANSAS

This State probably contains an abundance of clays of low and medium grade, but they have not as yet been systematically investigated. The formations yielding them are Carboniferous, Permian, Triassic, Cretaceous, Tertiary, and Pleistocene age.

Carboniferous

The Coal-measures underlie a rather extensive area in eastern Kansas, and consist of alternating strata of limestones, shales, and sandstones, with occasional coals. These beds dip gently to the westward, so that any one bed passes under the overlying ones if traced in that direction.

The shales of this series are mostly red-burning and at different localities have been found adapted to the manufacture of common and pressed brick, drain-tile, vitrified brick, and more recently even for roofing-tile and stoneware. They were first worked at Atchison in 1887, but since then factories have been opened up at Topeka, Pittsburg, Chanute, Coffeeville, etc. Those at Cherryvale are found immediately underlying the Independence limestone, while the beds worked at Iola overlie the Iola limestone. At Lawrence the beds utilized occupy a position near the middle of the Lawrence shales and right under the Oread limestone.

The Coal-measure shales of southeastern Kansas are ideally located, because of the supply of natural-gas fuel. The Permian outcrops to the west of the Coal-measures being found particularly in the Flint Hills area, and Haworth states that the shales are purer than those of the coal-measures.

Triassic

These occur in abundance, as at near Kingman, and Prosser states that they have been used for paint.

Cretaceous

The Dakota shales are well exposed near Salina, Dickinson County, but so far as known have not been utilized to any extent.

Pleistocene

The surface-clays are widely distributed over Kansas, but are chiefly important in the eastern portion. The gumbo clay, dug in many of the river valleys, has been burned in large quantities for railroad ballast.

REFERENCES ON KANSAS CLAYS

1. Grimsley, G. P., Kansas Mineral Products, 11th Bien. Rept., Kas. Board of Agric., 1897–98, p. 507, 1898.
2. Haworth, E., Annual Bulletins on Mineral Resources of Kansas, issued by Univ. Geol. Survey, as follows: 1899, p. 57; 1900 and 1901, p. 60; 1902, p. 40; 1897, p. 81; 1898, p. 61.
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4. Schrader, F. C., and Haworth, E., Clay Industries of the Independence District, U. S. Geol. Surv., Bull. 260, p. 546, 1905.
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KENTUCKY

Clays or shales of value for the manufacture of clay products are found in the Silurian, Mississippian, Pennsylvanian, Tertiary, and Pleistocene formations. In addition there are also residual clays derived from a number of the foregoing.

Silurian

This carries two shale formations, the Lulbegrud and Estill. The Lulbegrud shale, which outcrops in the Bluegrass region, is a smooth shale that weathers to a very plastic clay. It is usually not more than 15 feet thick, but should make good brick and drain-tile. The Estill shale is a bluish-gray smooth shale up to 100 feet thick, which overlies the former. It is suitable for brick and tile manufacture. Excellent exposures occur around Irvine. Both shales may be gypsiferous.

Mississippian

The New Providence shale occupies a curved belt extending from Jefferson County southward and eastward through Taylor and Lincoln counties, and then northeastward to Greenup County. It is a soft, usually greenish shale weathering to a plastic clay, and the fresh shale grinds up readily to a plastic mass. It varies from 75–100 feet in thickness and is the most widely utilized shale in Kentucky. The products made from it include common and pressed brick, paving-brick, hollow blocks, and common red earthenware.

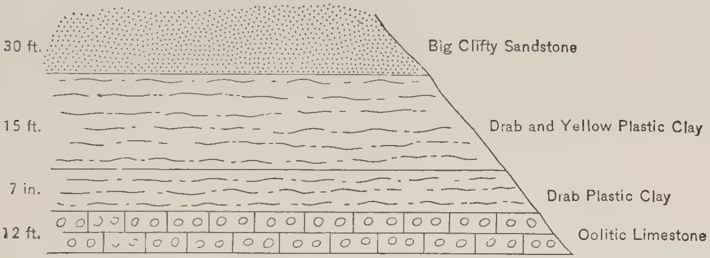

Fig. 124.—Section showing occurrence of Mississippian clays in Kentucky. (After Gardner, Ky. Geol. Surv., Bull. 6, 1905.)

The Rosewood shale which overlies the preceding is not quite as good but could be used for brick and hollow blocks. The Buffalo Wallow shales also of the Mississippian outcrop around the eastern border of the western coal field, but are less extensive than the New Providence. It is worked for red quarry tile and roofing-tile at Cloverport.

Analyses of Mississippian Clays

	I	II	III	IV
Silica (SiO_2)	54.07	48.09	44.16	43.64
Alumina (Al_2O_3)	22.60	34.66	37.34	34.57
Ferric oxide (Fe_2O_3)	5.04	.78	1.28	2.01
Lime (CaO)	.28	.27	.25	.99
Magnesia (MgO)	.50	.23	tr.	.10
Potash (K_2O)	4.61	.74	.53	.81
Soda (Na_2O)		.30		
Titanic acid (TiO_2)	.93	.25	tr.	tr.
Sulphur trioxide (SO_3)	.27	....	.31	.53
Loss on ignition	6.86	12.68	14.60	15.66
Moisture	4.62	2.39	2.82	2.71
Total	99.78	100.39	101.29	101.02

I. Plastic clay, J. B. Isaac place, 4 mi. S. E. of Bonnieville.
II. "Kaolin," P. Moss place, Bonnieville, Hart Co.
III. "Kaolin," 5 mi. S. E. of Bonnieville.
IV. "Kaolin," Hibernia, Taylor Co.
I–IV, from Bull. 6, Ky. Geol. Surv., 1905.

PENNSYLVANIAN

In Hancock County a shale, probably from the middle Pottsville, is worked for making sewer-pipe and flue-linings. In the eastern coalfield, notably in Boyd, Carter, Rowan, and Elliot counties, the Pottsville carries valuable deposits of fire-clays which form the basis of an important fire-brick industry. The clays are of three varieties, flint, plastic, and semi-hard. Olive Hill and neighboring towns are important localities of manufacture.

The following section will serve to show the relation of the clays in this district:

SECTION AT OLIVE HILL, CARTER COUNTY, KY

	Feet	Inches
1. Coal	....	2–6
2. No. 3 clay	1–9	....
3. Drab-flint clay	1–9	....
4. "Semi-hard" clay	1–5	....
5. "Pink-eye"	3	....
6. Blue shale	....	18–20
7. Iron ore	....	4–8
8. Maxville limestone	....	....

The one deposit may thus yield several varieties of clay. Tests and analyses of these clays are given below.

ANALYSES OF FIRE-CLAYS FROM NORTHEASTERN KENTUCKY

	I	II	III	IV	V
Silica (SiO_2)	43.82	43.76	58.34	39.56	47.08
Alumina (Al_2O_3)	39.67	40.21	33.34	43.35	36.12
Ferric oxide (Fe_2O_3)	1.09	.53	1.02	2.57	2.08
Lime (CaO)	1.43	.88	.72	.56	.86
Magnesia (MgO)	.11	.06	.36	.50	
Loss on ignition	11.96	14.12	6.13	13.09	13.75
Total	98.08	99.56	99.91	99.63	99.89
Cone of fusion	33	35–36	34–35	36	33

I. Semi-flint clay, Burnt House Mine, Olive Hill.
II. No. 1 flint clay. Burnt House Mine, Olive Hill.
III. Sandy or high silica flint clay. Replaces No. II around the outer edges of the lense-shaped deposits.
IV. "Aluminite." Olive Hill.
V. No. 2 plastic clay, Burnt House Mine, Olive Hill.
I–IV. Trans. Amer. Ceram. Soc., IX, p. 461, 1907.

Physical Tests of Kentucky Pottsville Fire-clays *

	I	II	III
Water of plasticity, per cent	16.8	14.6	17.5
Volume drying shrinkage	13.0	10.8	3.0

FIRING TESTS

Temperature, ° C.	Volume fire shrinkage, per cent	Average porosity	Volume fire shrinkage, per cent	Average porosity	Volume fire shrinkage, per cent	Average porosity
1050	11.5	29.0	13.5	25.8	19.7	25.3
1100	13.7	26.6	16.1	22.3	27.0	21.4
1150	18.2	23.3	19.5	20.0	23.7	20.4
1200	19.1	23.4	20.2	19.9	27.0	19.5
1250	19.1	22.6	20.5	19.4	21.3	22.9
1300	19.6	22.5	21.2	18.7	16.8	24.9
1350	20.6	21.4	21.7	17.5	14.0	25.9
1400	20.1	20.5	22.4	15.0	27.4	19.3
1450	23.9	18.9	23.1	14.4	....	....
1500	26.0	13.5	24.8	13.5	....	....
Cone of fusion.....	32–33	....	32–33	....	32	....

* Supplied by M. C. Booze, Mellon Institute, Pittsburg.

I. Soft and semi-flint clay.
II. Hard semi-flint clay.
III. Flint clay.

The Allegheny series of the eastern coalfield contains beds of plastic fire-clay which are worked to some extent but they are not as refractory as those in the Pottsville. At Madisonville in the western coalfield shales of this formation are worked for brick and tile, and in the eastern coalfield shales of the same series occur which could be made into buff brick, but the deposits are not very extensive.

In west-central Kentucky there are at the base of the Pottsville small deposits of Indianaite, of probably similar origin to those found in Huron County, Indiana.

Tertiary

The Lagrange formation of the Purchase region of western Kentucky contains a number of lenses of high grade, plastic refractory clays, many of which burn white. These are worked in a number of localities. The clays are of value in the manufacture of white ware, saggers, fire-brick, and other uses to which this type of clay is put. In Madison County the Irvine formation, probably of Tertiary age, carries small lenses of clay which are worked into stoneware and art pottery.

PHYSICAL TESTS OF KENTUCKY LA GRANGE CLAYS

	I	II
Water of plasticity, per cent	41.72	34.47
Linear air shrinkage, per cent	12.00	5.82
Modulus of rupture, pounds per square inch:		
Raw clay	25.55	189.1
Clay, sand 1 : 1	196.30	167.5

FIRING TESTS

Temperature, ° C.	Porosity, per cent	Volume fire shrinkage	Color	Porosity, per cent	Volume fire shrinkage	Color
1190	16.70	32.00	cream	18.33	28.30	cream, white
1250	16.79	29.89	cream	18.33	29.64	cream, white
1310	1.59	37.52	cream	10.84	33.41	cream, white
1370	.90	40.00	buff	.60	38.20	buff
1410	.30	38.00	buff	.40	37.50	buff
Cone of fusion	32			31		

I–II. From U. S. Geol. Surv., Bull. 708, 1922.

PLEISTOCENE

The surface loams in the Purchase region and alluvial deposits underlying river terraces in other parts of the State are widely used for the manufacture of common brick and drain-tile.

RESIDUAL CLAYS

These are found at a number of localities, but they are all ferruginous and are used almost solely for making common brick.

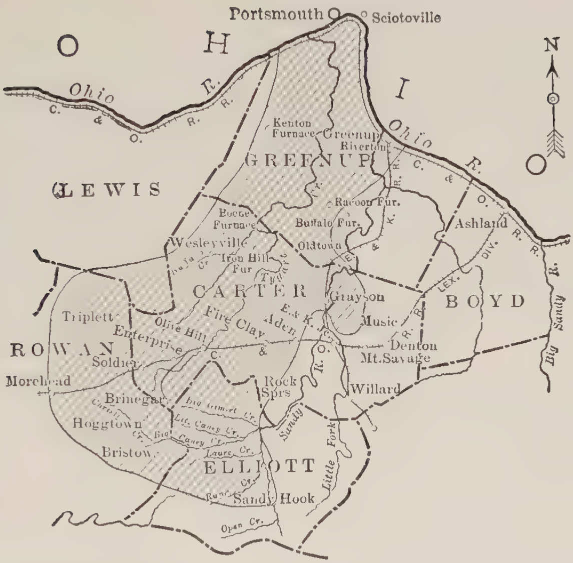

Fig. 125.—Map of Northeastern Kentucky, showing flint-clay area. After Greaves-Walker, Trans. Amer. Ceram. Soc., IX, 1907.)

Analyses of Some Kentucky Clays

	I	II	III	IV	V	VI	VII
SiO_2	58.82	54.33	44.16	39.56	47.08	41.00	59.50
Al_2O_3	18.14	19.44	37.34	43.35	36.12	37.22	24.96
Fe_2O_3	4.83	5.00	1.28	2.57	2.08	5.78	.72
CaO	.91	1.88	.25	.56	.86	.25	.32
MgO	1.74	2.22	tr.	.50		.46	.39
Na_2O	.36	.31	.53	....	....	.42	.28
K_2O	4.71	5.15					1.93
TiO_2	1.25	1.13	tr.	....	....	2.00	....
SO_3	.12	.39	.31	....	....	....	....
Ignition	6.12	7.80	14.60	13.09	13.75	13.60	11.87
Moist	1.98	2.20	2.82	....	....	....	....
	98.98	99.85	101.29	99.63	99.89	100.73	99.97

I. Lulbegrud shale, Irvine, Estill Co.
II. Estill shale, Panola, Madison Co.
III. So-called kaolin, same as Indianaite, from Pottsville formation, 5 miles S. E. of Bonnieville.
IV. Gibbsite bearing flint clay, called aluminite. Olive Hill.
V. Plastic fire clay, Olive Hill.
VI. Flint clay, Olive Hill district.
VII. White clay. 3 miles S. of Mayfield.

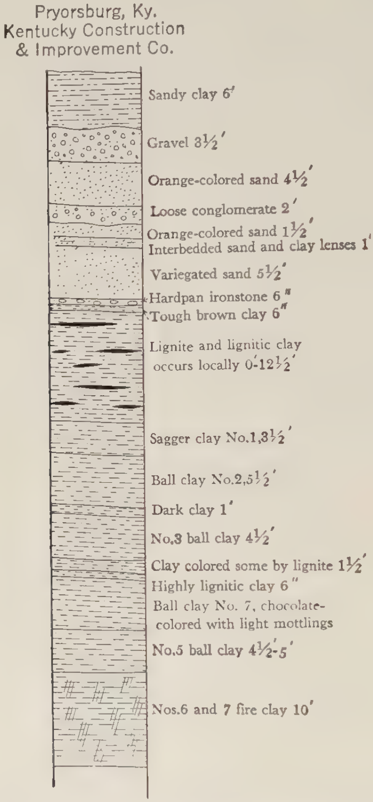

Fig. 126.—Section in Lagrange clays south of Mayfield, Ky. (U. S. G. S., Bull. 708, 1922.)

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2. Easton, H. D., Report on the Technology of Kentucky Clays, Including Chemical and Mechanical Analyses and Burning Tests, Ky. Geol. Surv., 4th ser., Vol. I, Pt. II, pp. 713–888, 1913.
3. Gardner, J. H., The Kaolins and Plastic Clays on the Eastern Rim of the Western Coalfield, Ky. Geol. Surv., Bull. 6, 1905.
4. Phalen, W. C., Clay Resources of Northeastern Kentucky, U. S. Geol. Surv., Bull. 285, p. 411, 1906.
5. Ries, H., Clays of Kentucky, Ky. Geol. Surv., 6th ser., 1912. Contains a complete bibliography.
6. Ries, H., Bayley, W. S., and others, High Grade Clays of the Eastern United States, U. S. Geol. Surv., Bull. 708, 1922.

LOUISIANA

The workable clays of Louisiana (Ref. 1) are all of transported character and post-Tertiary age. Three distinct types of clay are worked in Louisiana, and each of these is characteristic of that portion of the State in which it occurs.

The first, and oldest, is the Columbian mottle-gray clay of southeastern and southwestern Louisiana. It constitutes the " pine flats " of the coast, and the so-called " second bottoms " of the coastal plain. These clays have been worked at a number of points, especially along the Pearl, Chefuncte, and Sabine rivers.

" The second group includes clays of later Columbian age, skirting, though lying 30 to 50 feet above, the alluvial valley of the modern Mississippi River. Upon the eastern bank they form a continuous bluff from the Mississippi State line to Baton Rouge, thence bear southwestward to near Lake Mauripas as an escarpment bordering the modern Mississippi alluvium. Upon the immediate front, and extending some two or three miles back from the river, these yellow and somewhat loamy clays are covered by the brown loam or loess, and in such position have not been worked." But at Baton Rouge, where the loam has been largely removed, they are extensively dug for common brick.

Clays of similar character and geologic age form a somewhat interrupted escarpment on the western side of the present Mississippi Valley. These clays have been worked at Markville, Washington, and New Iberia, and utilized for tile, common brick, and dry-pressed brick. The heaviest and perhaps best of these deposits are found in West Carroll, Richland, and Franklin parishes.

The third group includes a series of pocket-like deposits in the modern alluvium of the Red River.

Near Shreveport, and further north in the bluffs of Caddo and Bossier parishes, are outcrops of lignite shales which may be of value.

REFERENCES ON LOUISIANA CLAYS

1. Clendenin, W. W., Clays of Louisiana, Eng. and Min. Jour., LXVI, p. 456, 1898.
2. Matson, G. C., Tests of Louisiana Clays, U. S. Geol. Surv., Bull. 660, 1917.
3. Ries, H., Report on some Louisiana Clay Samples, La. Exp. Stat., Pt. V, p. 263, 1899.

CHAPTER VIII

MAINE—NORTH CAROLINA

MAINE, NEW HAMPSHIRE AND VERMONT

The larger portion of these three States is underlain by either pre-Cambrian crystalline rocks or metamorphosed Paleozoic formations, consequently little clay is to be looked for in these. Covering the entire surface of these States, however, is a mantle of Pleistocene deposits, mostly glacial drift, which is employed at many places for the manufacture of bricks, as it often contains clayey members. None of the deposits are refractory, and indeed they may often be quite calcareous. The glacial clays are found in the till or have accumulated in hollows, but in addition to these are to be found in a series of estuarine deposits, represented by the clay-beds that have been formed in the larger valleys during a depression of the land in Pleistocene time. The subsequent uplift of the surface, and their erosion by streams, has left the clays as terrace deposits along the valleys. Deposits of this character are commonly more persistent and thicker than the preceding type of drift-clay.

In the Penobscot Bay region of Maine (Ref. 3) yellow, gray, and blue-gray clays of marine origin are found between sea-level and the 125-foot contour, and extending farthest inland along rivers and tidal estuaries. They are frequently from 15 to 35 feet deep, and sometimes even more. Their main use is for common brick. The following analyses are given by Bastin:

Analyses of Maine Brick Clays

	I	II	III
Silica (SiO_2)	62.80	62.33	61.59
Alumina (Al_2O_3)	17.36	17.70	19.10
Ferric oxide (Fe_2O_3)	4.40	5.19	7.53
Ferrous oxide (FeO)	2.00	1.72	
Lime (CaO)	.88	1.00	1.68
Magnesia (MgO)	1.58	1.53	1.87
Potash (K_2O)	3.05	2.41	....
Soda (Na_2O)	1.48	2.38	....
Titanic acid (TiO_2)	.87	.79	....
Ignition	4.39	3.81	5.51
Moisture	1.31	1.11	....
Total	100.12	99.97	97.28

I. Clay from brickyard. Thomaston, Me.
II. Hayden Point, nr. S. Thomaston, Me.
III. Brick-clay, near Rockland, Me.
I–III. U. S. Geol. Surv., Bull. 285, p. 30.

An extensive series underlies the terraces along the eastern shore of Lake Champlain, where they reach a height of several hundred feet above sea-level. These Pleistocene clays are mostly of value only for making common brick and drain-tile, although the smoother ones could be employed for red earthenware.

A rather important series of residual clays is found in Vermont in connection with limonite and manganese deposits. They have been recorded from Brandon, Monkton, and Bennington, as well as in Shaftsbury, Wallingford,[1] Plymouth, and Chittenden. Some of these are of white color, and although now used chiefly for paper manufacture, have also been tried for the manufacture of porcelain, stoneware, and firebrick. The following analyses show the composition of one from Forestdale, Vt.:

Analyses of Vermont Kaolins

	I	II
Silica (SiO_2)	53.70	48.91
Alumina (Al_2O_3)	35.12	39.99
Ferric oxide (Fe_2O_3)	0.06	0.33
Lime (CaO)	trace	0.34
Magnesia (MgO)	trace	....
Loss on ignition	10.55	8.92
Alkalies, by difference	0.57	1.51
Total	100.00	100.00

I. J. N. Nevius, analyst.
II. H. Carmichael, analyst.

A decomposed talcose schist known as "fire-clay" is worked near Rutland, and used for patent wall-plaster, stove-lining, etc.

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MARYLAND

The Maryland clay-deposits (Ref. 4) occur in formations ranging from Algonkian to Pleistocene, and the several formations of each system are each more or less limited to one of the three topographic provinces into which the State is divisible, as follows (Fig. 127):

Coastal Plain area, containing Pleistocene, Tertiary, Jura-Trias, and some of the Algonkian formations; bounded approximately on northwest by a line passing through Wilmington, Baltimore, and Washington.

Piedmont Plateau region, containing Paleozoic, Mesozoic, and pre-Cambrian formations. The first two yield shales, while the third gives a series of residual clays which may at times be of value. This region extends from the western boundary of the coastal plain to the Appalachian Mountains.

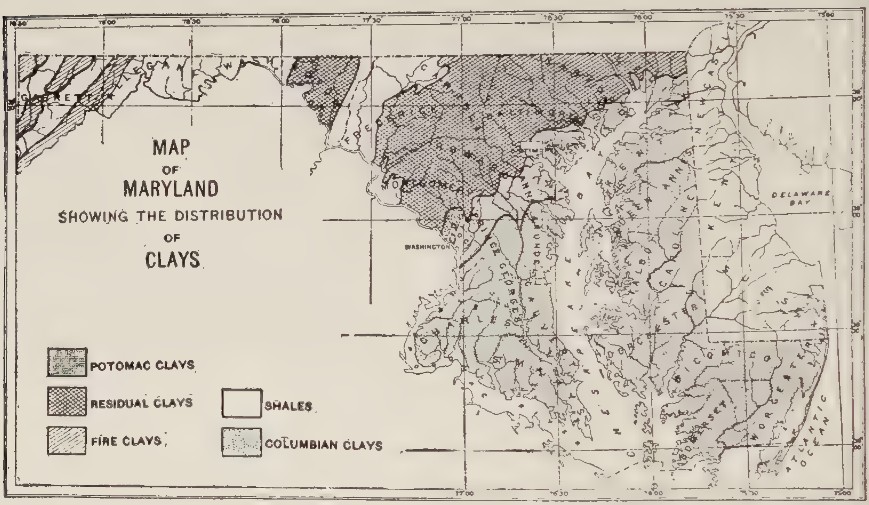

Fig. 127.—Map of Maryland, showing the distribution of clays. (After Md. Geol. Surv.)

Appalachian region, consisting of parallel mountain ridges composed of upturned Paleozoic strata. These are largely Devonian and Carboniferous shales which are abundant in Allegany and Garrett counties.

Algonkian Clays

These are exclusively of residual character and usually highly ferruginous; there are, however, in Cecil County a number of scattered kaolin deposits derived from feldspathic gneiss, and one near Northeast has been worked to some extent for use in paper manufacture. A second pit has been worked near Dorsey station in Howard County and used in fire-brick making.

The impure, ferruginous residuals, which have been derived from a variety of rocks and are all red-burning, vary in thickness, and except in the case of limestone residuals invariably pass by slow gradation into the parent rock below. They are widely distributed in the Piedmont area. A broad belt of limestone clay is prominent in Washington County.

SILURIAN SHALES

Most of these occurrences have no value for brick manufacture, unless they have at least partly weathered to residual clays. One good deposit occurs near the cement-works at Pinto, Allegany County.

DEVONIAN SHALES

These are represented in Allegany and Garrett counties by a great series of shales, sandy shales and shaly limestones. In some cases the shales have been so altered by folding that they develop little or no plasticity when ground and mixed with water, while at other times they are of excellent value for the manufacture of clay-products. The most important member is the Jennings shale, which is well exposed east of Cumberland and has been used for the manufacture of a red vitrified brick (Fig. 123).

CARBONIFEROUS

The Carboniferous formations are found in the western part of the State in Garrett and western Allegany counties. They are chiefly important because of the fire-clays which they contain.

Mauch Chunk.—This is a red shale with interbedded reddish sandstones, which at times weathers down to a plastic clay. The outcrops flank the ridges of western Allegany and eastern Garrett counties, but the beds are not worked.

Pottsville.—The fire-clay formerly placed in the Pottsville is now classed as Allegheny.

Allegheny.—The stratigraphy of western Maryland has been revised by C. K. Swartz, so that all the fire-clays formerly placed in the Pottsville are now classed as Allegheny. In this formation there are several beds of plastic and flint fire-clays some of which are very refractory (Ref. 6). Those worthy of mention are the following:

Mount Savage fire-clay.—This has been worked on Big Savage Mountain in the George's Creek basin where it is 5 to 12 feet thick. It occurs between the upper and lower Mount Savage coals, and consists of both plastic and flint fire-clay. The flint-clay occurs in lenses and irregular masses in the plastic material.

Ellerslie fire-clay (Lower Kittaning).—This overlies the Mount Savage sandstone. It is worked near Lonaconing and is known at several other localities.

Hardman fire-clay.—This occurs 125 to 150 feet above the base of the Allegheny formation in George's Creek Valley, and is 5 to 15 feet thick. It carries both plastic and flint-clay but is not as pure as the Mount Savage, although having a high fusing-point. It is worked at Mount Savage. Parts of it are non-refractory.

Bolivar clay.—The Davis or Upper Freeport coal is underlain locally by an impure fire-clay, which seems to correspond to the Bolivar of western Pennsylvania and eastern Ohio.

Conemaugh.—This formation carries the Thornton clay which has been used for brick in West Virginia. It occurs at a number of localities in Maryland.

The shales of this formation are usually argillaceous and sometimes associated with coal.

PHYSICAL TESTS OF MARYLAND FIRE CLAYS

	I	II	III	IV	V	VI
Water of plasticity, per cent....	16.9	17.9	....	....	17.4	22.7
Linear drying shrinkage, per cent	4.0	4.1	....	....	5.4	6.6
Slaking, minutes..............	4.6	3.5	....	....	6.4	9.0
Softening point, cone..........	30	22	33	28	26	18
Apparent porosity, per cent:						
1150° C................	23.4	17.9	25.0	24.4	18.1	38.7
1200° C...............	19.3	12.3	26.2	20.8	13.9	38.2
1300° C................	14.9	11.3	27.7	18.9	4.0	40.0
1400° C................	12.1	6.4	26.3	14.0	8.2	40.5
Volume shrinkage, per cent:						
1150° C................	7.8	15.9	15.9	4.5	12.2	2.0
1200° C................	9.2	17.4	17.9	4.4	15.1	2.6
1300° C................	9.3	15.3	18.6	3.9	18.9	−1.3
1400° C................	6.7	10.6	14.0	3.9	4.3	−4.4

I. Mount Savage or Clarion plastic clay.
II. Mount Savage or Clarion plastic clay.
III Mount Savage or Clarion flint clay.
IV. Mount Savage or Clarion flint clay.
V. Ellerslie (Lower Kittanning) plastic clay.
VI. Hardman, flint clay.

From Md. Geol. Surv., Vol. XI, Pt. II, 1922.

CRETACEOUS AND JURA-TRIAS CLAYS

The clay-deposits of these two ages underlie large areas in eastern Maryland and are perhaps the most important clay series in the State. They are divisible into the following groups:

Upper Cretaceous	Rancocas	
	Monmouth	
	Matawan	
Lower Cretaceous	Raritan	Potomac Group.
	Patapsco	
Jura Trias	Arundel	
	Patuxent	

The Upper Cretaceous deposits of Maryland are a continuation of similar beds in Delaware and New Jersey and cross the State from northeast to southwest, being especially developed in Cecil, Kent, Anne Arundel, and Prince George counties. In Maryland, however, these deposits carry but little clay. Those of the Potomac Group or Lower Cretaceous are of much importance, and consist of a series of sand, sandy clays, and gravels which have been deposited at different periods and under various conditions, the result being that the most unlike materials pass into each other horizontally. The characters of the several subdivisions of the Potomac together with their uses are as follows:

Patuxent.—This is best developed in the upper valleys of the Big Patuxent and Little Patuxent rivers and is sometimes found resting on the crystalline rocks of the Piedmont Plateau. It is traceable as a narrow, irregular, and sometimes broken belt from Cecil County on the northeast across Harford, Baltimore, Anne Arundel, and Prince George counties to the border of the District of Columbia. The Patuxent at times contains beds of refractory clay, the best occurrences having been noted around Baltimore and near Sewell in Harford County. The clays, which commonly show low tensile strength and low air- and fire-shrinkage, have been used with much success for admixture with the more plastic Arundel clays in the manufacture of terra-cotta.

Arundel formation.—Although highly developed in Anne Arundel County, the deposits of this horizon can be traced as a broken belt from Cecil County to the District of Columbia. The deposits form a series of large and small lenses of clays bearing carbonate iron ore (Fig. 26) which have commonly been deposited in old depressions in the surface of the Patuxent formation. They vary considerably in size, ranging from a few feet up to 125 feet, and are usually made up of a blue, often siliceous clay of good plasticity but not high tensile strength. Cecil, Harford, Anne Arundel, Howard, Prince George, and Baltimore counties all contain many beds of Arundel clay. They are mostly red-burning and so their chief use has been for the manufacture of common and pressed brick, but some has been dug near Baltimore for making sewer-pipe and common pottery, in fact refractory clay is at times found and used for terra-cotta.

Patapsco formation.—The type exposures of this are on the shores of the Patapsco River, although the formation extends across the State. The clays are chiefly bright-colored, mottled materials, which are often surrounded by sand-deposits. At the base of the formation there is often a bed of bluish stoneware clay, which is worked in Cecil County.

Raritan formation.—The beds in this formation are predominatingly sandy, and although at times they contain lenses of clay they are of far less importance than those in New Jersey.

TERTIARY CLAYS

An important bed of red clay of Tertiary age extends from the South River southwestward, showing many outcrops, especially along the Western and Charles branches of the Patuxent, at Upper Marlboro in the Potomac Valley, in Prince George County, etc. It is a somewhat fine-grained plastic clay, at least 20 feet thick, and burns to a good hard red body, but is not worked, although it could be used for pressed brick.

PLEISTOCENE

This overlies the earlier formations of the coastal plain, and in some cases extends up on the rocks of the Piedmont Plateau, forming a mantle of sandy clay, loam, and gravel of varying thickness. The loams, which belong to the Columbia formation, are very extensive and form an abundant source of brick material, being much used for this purpose around Baltimore.

Occasionally the Pleistocene carries stoneware clays, as along Chesapeake Bay south of Bodkin Point.

The physical properties and chemical composition of clays from the different formations are given below, all of them being taken from Volume IV of the Maryland Geological Survey:

ANALYSES OF MARYLAND CLAYS

	I	II	III	IV	V	VI
Silica (SiO_2)	70.25	56.15	75.40	69.40	59.70	68.30
Alumina (Al_2O_3)	17.71	33.295	16.73	19.70	27.00	21.27
Ferric oxide (Fe_2O_3)	4.10	0.59	1.27	2.00	2.10	1.43
Lime (CaO)	0.70	0.17	0.35	0.20	0.60	0.52
Magnesia (MgO)	0.40	0.115	0.90	0.60	0.52	0.80
Alkalies (Na_2O, K_2O)	1.76	....	0.50	0.62	1.96	0.20
Ignition	4.80	9.68	5.30	7.85	8.20	7.55
Total	99.72	100.00	100.45	100.37	100.08	100.07

	VII	VIII	IX	X	XI	XII
Silica (SiO_2)	72.50	55.65	61.00	46.10	58.60	67.50
Alumina (Al_2O_3)	17.00	30.53	26.36	38.05	28.71	17.20
Ferric oxide (Fe_2O_3)	1.50	0.97	0.83	1.05	3.22	6.70
Lime (CaO)	0.35	0.75	0.21	0.39	0.40	0.45
Magnesia (MgO)	0.60	0.60	0.10	0.60	0.35	....
Alkalies (Na_2O, K_2O)	1.10	0.20	trace	....	0.63	1.76
Ignition	6.50	12.30	11.60	12.95	8.90	5.90
Total	99.55	101.00	100.10	99.14	100.81	99.51

LOCALITIES OF THE ABOVE

No.	Locality	Geological age	Uses
I	Bottom shale, brick works, Cumberland, Allegany County	Devonian	Paving-brick
II	Flint-clay, Mount Savage, Allegany County	Carboniferous	Fire-brick
III	Baldwin's sand-pit, Raritan River, Anne Arundel County	Raritan	Not worked
IV	Bodkin Point, Anne Arundel County	Pleistocene	Not worked
V	Baltimore, Baltimore County	Arundel	Brick
VI	Link's pit, south of Baltimore, Baltimore County	Arundel	Terra-cotta
VII	Carpenter Point, Cecil County	Patapsco	Stoneware
VIII	Northeast, Cecil County	Algonkian	Kaolin
IX	Flint-clay, Swallows Falls, Garrett County	Carboniferous	Not worked
X	Shale, Swallows Falls, Garrett County	Carboniferous	Not worked
IX	Upper Marlboro, Prince George County	Eocene	Not worked
XII	Residual limestone clay, Williamsport, Washington County	Pleistocene	Bricks

PHYSICAL TESTS OF MARYLAND CLAYS

	I	II	III	IV	V	VI
Per cent water required	19	30	40	19	22.5	23
Air-shrinkage, per cent	4	6	11	4	6	6
Fire-shrinkage	5	4	9	6	9	10
Average tensile strength, pounds per square inch	55	40	223	65	77	110
Cone of incipient fusion	01	8	05	3	1	01
vitrification	4	27+	2	8+	6	8
viscosity	7	......	7	......	10	12
Plasticity	lean	good	high	fair	good	high

	VII	VIII	IX	X	XI	XII
Per cent water required	20	30	18	20	25	35
Air-shrinkage, per cent	2	6	1.5	5	4	9
Fire-shrinkage	4	4	12.5	3.5	5	11
Average tensile strength, pounds per square inch	10	40	20	100	15	132
Cone of incipient fusion	27	8	10	3	27+	05
vitrification	......	27+	27	8	......	6
viscosity	......	......	......	10+	......	10
Plasticity	lean	fair	lean	fair	lean	fair

LOCALITIES OF THE ABOVE

No.	Locality	Geological age	Uses
I	Savage Mountain, Allegany County	Mauch Chunk	Not worked
II	Bodkin Point, Anne Arundel County	Pleistocene	Not worked
III	Two miles south of Bodkin Point, Anne Arundel County	Pleistocene	Not worked
IV	One-half mile south of Harman, Anne Arundel County	Raritan	Dry-pressed brick
V	Link-pit, Baltimore, Anne Arundel County	Arundel	Terra-cotta
VI	Near Elkton, Cecil County	Patapsco	Stoneware
VII	Leslie, Cecil County	Residual	Stove-lining
VIII	Northeast River, Cecil County	Patapsco	Not worked
IX	Northeast, Cecil County	Residual	Paper-clay
X	Shannon Hill, Cecil County	Patapsco	Not worked
XI	Dorsey, Howard County	Residual	Fire-brick
XII	Upper Marlboro, Prince George County	Eocene	Not worked

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MASSACHUSETTS

Most of the clays dug in the State are obtained from the Pleistocene formations, while comparatively small amounts are taken from the Cretaceous and Tertiary strata, and residual clays are rare.

Residual Clays

Two deposits of white residual clay or kaolin have been recorded from Massachusetts. One of these is at Blandford, Hampden County; the other is 4 miles south of Clayton, Berkshire County. The first has originated by the decomposition of a pegmatite vein in mica-schist, and has a width of nearly 100 feet.[1] It has been used for the manufacture of white brick and terra-cotta. The second has been derived from feldspathic quartzite or gneiss, and in its crude state is lean and sandy. The following analyses represent the composition of washed samples of the Blandford (I), and of Clayton (II) materials.[2]

Analyses of Massachusetts Kaolins

	I	II
Silica (SiO_2)	52.03	50.00
Alumina (Al_2O_3)	31.76	44.00
Ferric oxide (Fe_2O_3)	trace	....
Ferrous oxide (FeO)	....	1.00
Lime (CaO)	trace	.024
Magnesia (MgO)	.54	....
Alkalies (Na_2O,K_2O)	trace	1.24
Water (H_2O)	15.55	....
Total	99.88	96.264

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[1] Crosby, Technol. Quart., III, 1890.

[2] This evidently represents the composition of the burned clay. The analyst is unknown.

Residual clays are known in Essex County, but are of no commercial value. One bed of fine white kaolin derived from felsite occurs on the west side of Kent's Island, Newbury. Another mass is found in South Lawrence, but neither have been worked, as they are too small.

CRETACEOUS AND TERTIARY CLAYS

The Cretaceous and Tertiary beds form a thick series of clays and sands, well exposed in the Gay Head cliffs. The clay-deposits are pockety, owing partly to the frequent changes of conditions during deposition, and partly to their subsequent disturbance by the ice of the continental glacier as it advanced southward. These clays have been used to a slight extent for bricks, and somewhat for souvenir pottery.

PLEISTOCENE CLAYS

These form the most important clay resource of the State, but contain no high-grade materials. They are extensively developed on the islands of Martha's Vineyard, Nantucket, and in southeastern Massachusetts on Cape Cod, but most of these are not well adapted to brick manufacture, as they vary too much in burning.

The true glacial clays are found and worked at many points. (Ref. 6.) Some of these were formed in estuaries, others in pools under or in front of the ice, while still others occur in the morainal drift and represent ground-up rock-flour. In the region south and east of a line from the mouth of the Merrimac River to Stonington, Conn., they are not found above an elevation of 100 feet. Around Boston these glacial clays are well developed in the estuaries of the Charles, Mystic, and Saugus rivers north and west of Boston. The clays are bluish, plastic, and very fine, but may at times contain bowlders or scattered pebbles.

Similar clays are extensively worked along the Mystic River at Medford; at Cambridge and Belmont on the Charles River; at Holyoke and South Hadley on the Connecticut; and at Taunton on the Taunton River. They are used chiefly for common-brick manufacture. There are but few published analyses of Massachusetts clays. Of the two given p. 457, No. I is a glacial clay from West Cambridge, J. Card, analyst, and No. II a red clay from south end of Gay Head section. (7th Ann. Rept., U. S. Geol. Surv., p. 359.)

Analyses of Massachusetts Clays

	I	II
Silica (SiO_2)	48.99	57.50
Alumina (Al_2O_3)	28.90	31.21
Ferric oxide (Fe_2O_3)	3.89	....
Lime (CaO)	7.1	0.19
Magnesia (MgO)	3.66	0.20
Alkalies (Na_2O,K_2O)	4.73	0.40
Water (H_2O)	3.31	9.83
Total	100.58	99.33

In Essex County, in which brickmaking began over two hundred years ago, Pleistocene surface-clays are much used for bricks and pottery. They are of variable thickness, some exceeding 30 feet in depth, and are worked at Danversport, Haverhill, Beverly, and Salem. Some of the deposits are excavated below sea-level.

It is interesting to note the variety of products made from these common surface-clays, for they include common and pressed brick, fireproofing, and earthenware. A fine pottery is made at Newburyport from a mixture of local clay and Ohio clays.

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MICHIGAN

The clays of Michigan are obtained from two types of deposits: (1) Shales of Palæozoic age, and (2) surface clays of lake, river or glacial origin. These surface clays and associated deposits form a rather extensive mantle which often hides the bed-rock.

PALEOZOIC SHALES

The shale formations which underlie a large part of the Southern Peninsula form a large basin, with the younger formations occupying the center (Fig. 128). Although they underlie a large area there are few outcrops on account of the heavy mantle of glacial drift and lake deposits. The age of these shales ranges from Silurian to Carboniferous, and their characters are as follows:

Bell shales.—A soft blue shale, 50 to 80 feet thick, which outcrops in different places in Cheboygan and Presque Isle counties. It is fine grained, plastic, red-burning and probably suitable for brick and tile.

Antrim-Bedford shales.—These shales which belong to the upper Devonian, are black at the bottom and generally blue at the top. Concretions of siderite and pyrite are not uncommon. Both shales burn to a hard red product suitable for brick and tile, but the lower one must be carefully oxidized in firing.

They outcrop in many places throughout the northern counties.

Coldwater shales.—These shales which belong to the Mississippian are blue and gray with large concretions of siderite and lenses of sandstone especially near the top. The shales are 700 to 1000 feet thick and while not used for clay products are said to be suitable for brick and tile manufacture.

Coal-measure shales.—This includes a number of shale-beds which are said to be suitable for brick and tile. The white shale (so-called fire-clay) of the Saginaw formation is classed as semi-refractory and stated to be suitable for making sewer-pipe and paving-brick.

SURFACE CLAYS

The surface clays of Michigan are of three types: (1) Morainic or drift clays; (2) Lake clays; and (3) River silts.

The morainic or drift clays are usually stony (Fig. 131) and run high in lime carbonate or limestone pebbles, and occur in both the northern and southern peninsula. They are as a rule suitable only for common brick.

The lake clays have about the same composition and burning properties as the morainic clays, but contain fewer stones and are more workable. In the southern peninsula they are confined almost entirely to a strip 40 miles wide extending from the Ohio line northward along the east side of the peninsula, and around Saginaw Bay. Extensive deposits occur in the northern peninsula in Ontanagon, Houghton, and Baraga counties. The lake clays are often calcareous and may be used for brick and tile. Some of the deposits in Ontanagon County are of value as slip-clays. Fullers' earth occurs in the lake deposits near Petoskey.

The river silts are generally sandy, but fairly free from pebbles. They are often suitable for brick or tile.

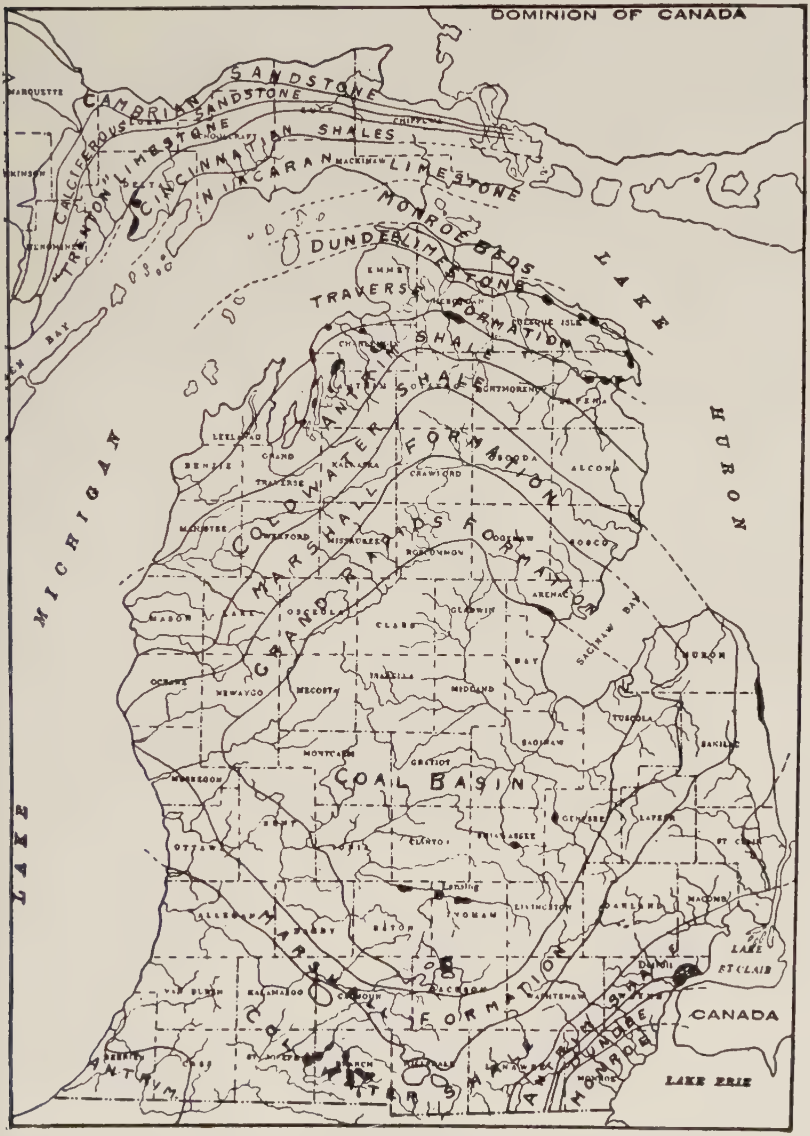

Fig. 128.—Map of Michigan showing distribution of hard rock formations and the areas (solid black) in which exposures of shale occur. (After Brown, Mich. Geol. Surv., Pub. 36, 1924.)

Tests of Michigan Clays and Shales

		I	II	III	IV	V	VI	VII	VIII	IX	X	XI
Water plasticity, per cent		26.4	21.4	31.0	23.7	28.4	25.5	26.2	20.8	20.9	30.3	33.1
Linear air shrinkage, per cent		4.9	5.0	9.7	7.6	9.5	5.0	7.6	4.5	3.0	7.7	9.7
Average tensile strength, pounds per square inch		70	181	145	100	140	....	85	40	175	47	70
Cone 010	Porosity, per cent	....	35.5	33.3	45.0	39.0	43.9	35.0	....	....	34.3	32.3
	Linear fire shrinkage, per cent	....	−1.7	1.2	−5.4	2.1	−0.7	0.2	....	....	0.0	−1.1
	Color	....	lt. red	sal. pink	salmon	salmon	salmon	salmon	....	....	salmon	tan
Cone 08	Porosity, per cent	....	29.3	34.6	47.5	39.6	42.5	33.6	34.7	61.2	33.1	31.6
	Linear fire shrinkage, per cent	....	−1.4	0.4	−3.9	1.8	−0.7	1.1	0.2	−0.4	1.9	1.1
	Color	....	lt. red	sal. pink	crm.sal.	cream	salmon	lt. red	salmon	pink	salmon	tan
Cone 06	Porosity, per cent	33.10	27.6	34.0	49.5	41.0	39.6	32.3	35.9	65.9	29.8	26.8
	Linear fire shrinkage, per cent	0.90	1.0	0.4	−3.4	1.8	0.7	1.1	0.2	.0.	4.5	3.7
	Color	salmon	lt. red	sal. pink	cream	cream	salmon	lt. red	salmon	pink	salmon	lt. red
Cone 04	Porosity, per cent	29.8	23.8	32.9	50.0	39.9	34.7	25.7	34.4	59.7	21.4	18.3
	Linear fire shrinkage, per cent	2.3	2.0	0.9	−4.6	2.3	3.2	4.1	0.8	−1.0	7.4	7.4
	Color	lt. red	red	sal. pink	cream	cream	red	red brn.	salmon	pink	red	red
Cone 02	Porosity, per cent	20.2	18.7	18.3	49.2	37.1	25.6	15.7	31.2	57.0	8.1	0.9
	Linear fire shrinkage, per cent	6.0	3.5	6.0	−2.1	3.8	6.9	6.9	3.2	0.9	8.9	10.0
	Color	deep red	dk. red	lt. brn.	cream	cream	dk. red	red brn.	salmon	pink	dk. red	dk. red
Cone 1	Porosity, per cent	8.8	15.4	0.9	49.2	22.8	15.6	6.2	26.5	54.4	1.7	0.8
	Linear fire shrinkage, per cent	9.6	4.7	10.6	−1.6	8.4	....	7.8	4.3	3.0	11.5	8.7
	Color	choc.brn.	dk. red	dk. brn.	cream	olive	dk. red	dk. brn.	red	lt. brn.	choc.	brown
Cone 3	Porosity, per cent	4.0	12.6	....	39.2	4.9	8.2	4.4	26.5	54.3	0.09	1.4
	Linear fire shrinkage, per cent	9.7	4.8	visc.	9.4	13.2	11.1	5.9	4.9	4.1	11.8	2.8
	Color	choc.	choc.	....	lt. olive	olive	choc.	dk. brn.	red brn.	lt. brn.	choc.	dk. brn.
Cone 5	Porosity, per cent	4.5	5.1	....	6.1	2.0	5.8	....	21.1	53.8	0.09	8.8
	Linear fire shrinkage, per cent	7.0	4.8	....	15.0	14.0	11.0	visc.	6.1	3.9	11.5	0.9
	Color	choc.	choc.	....	olive	olive	choc.	....	red brn.	brown	choc.	dk. brn.
Cone 7	Porosity, per cent	2.8	2.1	....	....	4.1	5.6	....	19.2	52.8	0.65	....
	Linear fire shrinkage, per cent	6.0	4.8	....	visc.	8.7	11.0	....	5.7	5.9	5.6	visc.
	Color	choc.	choc.	....	....	olive	choc.	....	red brn.	brown	choc.	....
Cone 9	Porosity, per cent	3.8	....	....	....	....	1.4*	....	14.8	47.8	17.6	....
	Linear fire shrinkage, per cent	2.3	....	....	....	....	6.0*	....	2.2	7.8	−0.6	....
	Color	dk. choc.	....	....	....	....	choc.	....	br. gray	gray	choc.	....
Cone 11	Porosity, per cent	....	....	....	....	....	....	....	....	45.2	....	....
	Linear fire shrinkage, per cent	....	....	....	....	....	....	....	....	3.1	....	....
	Color	....	....	....	....	....	....	....	....	gray	....	....
Cone 13	Porosity, per cent	....	....	....	....	....	....	....	....	48.0	....	....
	Linear fire shrinkage, per cent	....	....	....	....	....	....	....	....	1.1	....	....
	Color	....	....	....	....	....	....	....	....	gray	....	....
Hard, cone		02	04	02	3	1	04	04	1	02	04	06

* Cone 8.

See page 461 for Column Headings I–XI.

I. River silt, Allegan, Mich.
II. Lake clay, Azalia, Monroe Co.
III. Lake clay, Munising, Alger Co.
IV. Boulder clay, Menominee, Menominee Co.
V. High lime boulder clay, Gladwin, Gladwin Co. Used for stiff mud brick.
VI. Antrim shale, 3 miles S. of Indian River. Cheboygan Co. Heated 5 hours at 750° C. to oxidize carbon.
VII. Bedford shale, Ellsworth, Antrim Co.
VIII. Coal measure shale, Grand Ledge, Eaton Co. Used for face brick.
IX. White Coal-measures clay, Auburn, Bay Co.
X. Coldwater shale, Coldwater, Branch Co. Carbonaceous, oxidized 2½ hours at 750° C.
XI. Bell shale, Rogers City, Presque Isle Co.
All from Mich. Geol. Surv., Pub. 36, Geol. Ser. 30, 1924.

ANALYSES OF MICHIGAN CLAYS AND SHALES

	I	II	III	IV	V
Silica (SiO_2)	55.30	44.30	56.50	53.44	55.95
Alumina (Al_2O_3)	14.20	23.72	19.31	24.80	17.43
Ferric oxide (Fe_2O_3)	3.62	7.68	5.89	0.76	7.67
Lime (CaO)	0.30*	1.11	1.00*	0.25	2.14*
Magnesia (MgO)	2.61†	1.50	1.85†	....	1.55†
Potash (K_2O)	2.15	2.00	5.98	20.75	2.86
Soda (Na_2O)					
Carbon dioxide (CO_2)	....	2.36	....		
Water (H_2O)	21.82	17.64	9.47		12.40
+Organic					

	VI	VII	VIII	IX	X
Silica (SiO_2)	61.09	54.62	44.15	41.86	52.92
Alumina (Al_2O_3)	19.19	12.82	10.00	10.70	12.25
Ferric oxide (Fe_2O_3)	6.78	2.00	4.08	5.02	6.45
Lime (CaO)	2.51	13.68	24.64*	14.33*	13.84*
Magnesia (MgO)	0.65	4.25	1.50†	2.81†	3.55†
Potash (K_2O)	3.16	12.01	1.55	2.80	3.35
Soda (Na_2O)					
Carbon dioxide (CO_2)	....		....	14.50	....
Water (H_2O)	5.13		12.13	8.00	7.14
+Organic	SO_2 1.42	....	1.95	....	....

* = $CaCO_3$. † = $MgCO_3$.

REFERENCES ON MICHIGAN CLAYS

1. Brown, G. G., Clays and Shales of Michigan and Their Uses, Mich. Dept. Conserv., Geol. Surv. Div., Pub. 36, Geol. Ser. 30, 1924.
2. Ries, H., Clays and Shales of Michigan, Mich. Geol. Surv., VIII, Pt. I, 1900.

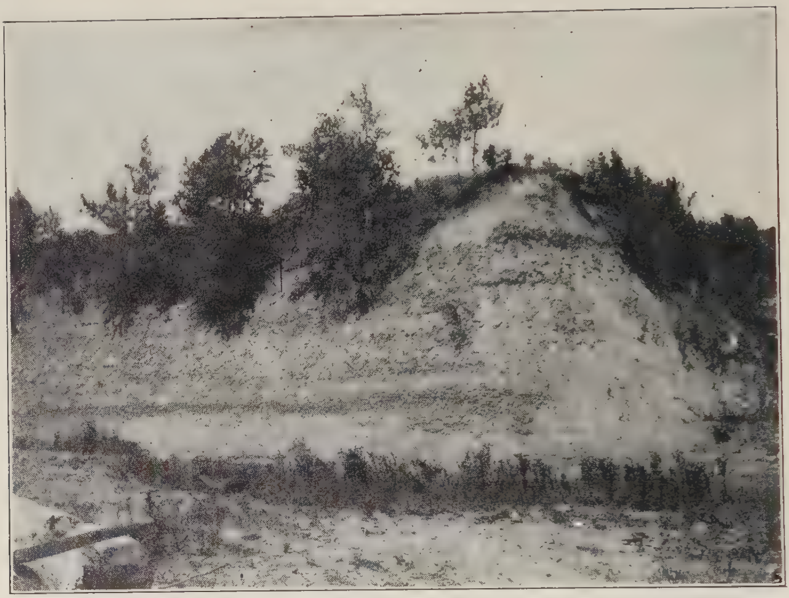

FIG. 129.—Coldwater (Carboniferous) shales at White Rock, near Forestville, Mich. (After H. Ries, Mich. Geol. Surv., VIII, Pt. I, p. 44, 1900.)

FIG. 130.—Carboniferous shale used for paving-brick, Flushing, Mich. (After H. Ries, Mich. Geol. Surv., VIII, Pt. I, p. 29, 1900.)

MINNESOTA

Clay-bearing formations.—The clay-bearing formations of Minnesota include: Residual deposits from Archean rocks, Algonkian, Ordovician, Cretaceous, Pleistocene, and Recent.

RESIDUAL DEPOSITS

In the southwestern part of the state the Archean granites and granite gneisses are covered by residual clay which is the result of pre-Cretaceous weathering and in most places is overlain by Cretaceous sediments. Much of the material is said to be a white highly refractory clay which could be used for whiteware manufacture.

ALGONKIAN

Beds of shale occur in several of the pre-Cambrian formations but the material is too much metamorphosed and usually too sandy to be of much value.

ORDOVICIAN

The Decorah shale which outcrops in the southeastern part of the State is of much value. It is 50 to 100 feet thick and contains layers and lenses of limestone interbedded with the shale, but there is usually a 10-foot bed of shale at the bottom of the formation. The ground shale yields a greenish plastic clay which is used extensively near St. Paul and in Goodhue County, for making pressed brick, common brick, drain-tile, etc.

CRETACEOUS

Basal Cretaceous clays are most prominently exposed in the bluffs on both sides of the Minnesota River from Granite Falls to New Ulm. They are mostly pebbly or with concretions, of highly refractory character, but are not used. Cretaceous shales are thought to underlie much of the western part of the State, and also occur in patches in the southeastern portion. The shales are usually light to dark gray and are interbedded with sandstone and less commonly limestone, but are exceedingly plastic. They are used in Goodhue and LeSueur counties for stoneware (Fig. 132), common brick and hollow brick. In the western part of the State these shales are deeply covered by drift.

PLEISTOCENE

Gray glacial drift, consisting mostly of clay, weathered yellow at the surface, covers rather more than the western half of the State. Special treatment of this clay is necessary on account of the presence of limestone pebbles which must be either ground up or screened out before the clay is used. It is employed for common brick and drain-tile.

Gray laminated lake and river clays occur chiefly along the valleys of the Minnesota and Mississippi rivers. The material is used for common brick but is not suitable for vitrified products.

Red drift clay is found in the eastern part of the State. North of Minneapolis it is used for common brick, face brick, and hollow brick, and much of it could be used for paving-brick.

Red laminated lake and river clays are found along the eastern border of the State, and extend into Wisconsin. They are red-burning but are not much used in Minnesota.

Loess is found in the southeastern part of the State and to some extent in the southwestern portion. It is 2–4 feet thick on the uplands but much thicker in the valleys. While not used alone, at a number of localities it is mixed with the underlying clay for use.

Recent alluvial clays are found chiefly along the Red and Minnesota rivers. Some of the Red River alluvial clay may have been deposited in Glacial times. Of the Red River clay only the leached, yellow upper portion can be used for brickmaking, as the lower part not only has too high a shrinkage but is also too highly calcareous.

The following tables give the chemical composition and physical properties of some of the Minnesota clays:

Chemical Analyses of Some Minnesota Clays

	I	II	III	IV
SiO_2	56.35	69.92	47.70	50.51
Al_2O_3	18.63	17.39	13.58	15.89
Fe_2O_3	6.19	1.68	6.51	8.21
FeO				
CaO	.96	.60	11.70	7.10
MgO	2.97	1.11	3.13	5.14
Na_2O	.25	.07	1.05	1.66
K_2O	7.37	2.25	2.34	1.87
Moisture	2.41	1.10	1.79	2.44
Ignition	4.81	5.45	13.23	7.35
TiO_2	.65	.63	.31	.26
	100.59	99.99	101.34	100.43

I. Decorah shale, West St. Paul, F. F. Grout, analyst.
II. Stoneware clay, Redwing, Goodhue Co., F. F. Grout, analyst.
III. Gray laminated clay, Net Lake Rapids, A. W. Ganger, analyst.
IV. Red Lake clay, Carlton Co., A. W. Ganger, analyst.
All analyses from U. S. G. S., Bull. 678.

PHYSICAL TESTS OF MINNESOTA CLAYS

	Number of tests	Slaking time, minutes	Plasticity	Water of plasticity, per cent	Tensile strength, pounds per square inch	Linear air shrinkage, per cent	Fusion		Range of vitrification, ° F.	Linear fire shrinkage		Absorption	
							Incipient ° F.	Viscous ° F.		At incipient fusion, per cent	At viscosity, per cent	At incipient fusion, per cent	At viscosity, per cent
Archean residual clay	4	2	lean	....	30	4	2138	2800	700	2	5	20	10
Cambrian shale	6	many	lean	18	40	3	1994	2246	252	0	3	20	8
Decorah shale	15	5	very high	30	125	8	1778	2102	324	4	6	15	7
Cretaceous:													
Basal clay	10	many	lean	26	50	4	2282	3150	900	3	6	19	6
Buff-burning shale	10	4	fair	22	170	6	1886	2462	576	1	5	16	5
Red-burning shale	15	3	high	29	160	8	1814	2210	396	2	7	15	5
Pleistocene:													
Gray drift	25	2	high	24	150	8	2030	2174	144	1	6	21	6
Gray laminated clay (south)	50	2	fair	27	120	5	1994	2174	180	1	8	25	7
Gray laminated clay (north)	10	6	high	33	160	9	1958	2174	216	1	8	20	1
Silt of Red River Valley	10	3	high	32	120	8	1994	2174	180	1	8	24	8
Red drift	7	2	fair	20	140	4	1958	2174	216	1	6	15	4
Red laminated clay	5	1	low	21	80	4	1958	2138	180	1	9	20	2
Red clay of Lake Duluth	5	2	very high	40	60	10	1814	2102	288	3	12	19	2
Outwash	5	1	low	25	120	4	2030	2246	216	1	8	20	4
Loess	5	1	low	23	170	3	2030	2246	216	1	7	20	3
Recent:													
River clay	10	1	fair	25	130	5	2030	2210	180	1	7	21	6
Lake and swamp clay	20	2	high	28	140	6	1958	2174	216	1	7	20	3

All from U. S. Geol. Survey, Bull. 678.

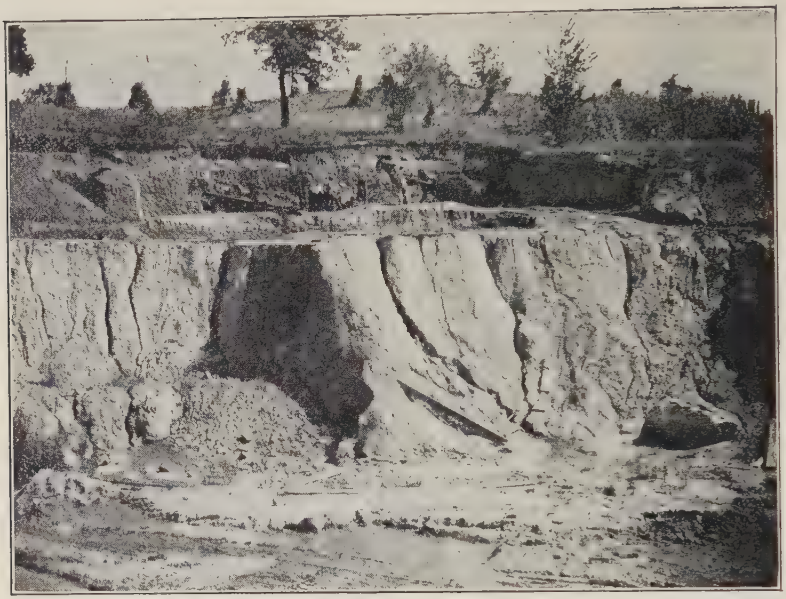

FIG. 131.—Deposit of calcareous glacial clay, Ionia, Mich. (After H. Ries, Mich. Geol. Surv., VIII, Pt. I, p. 52, 1900.)

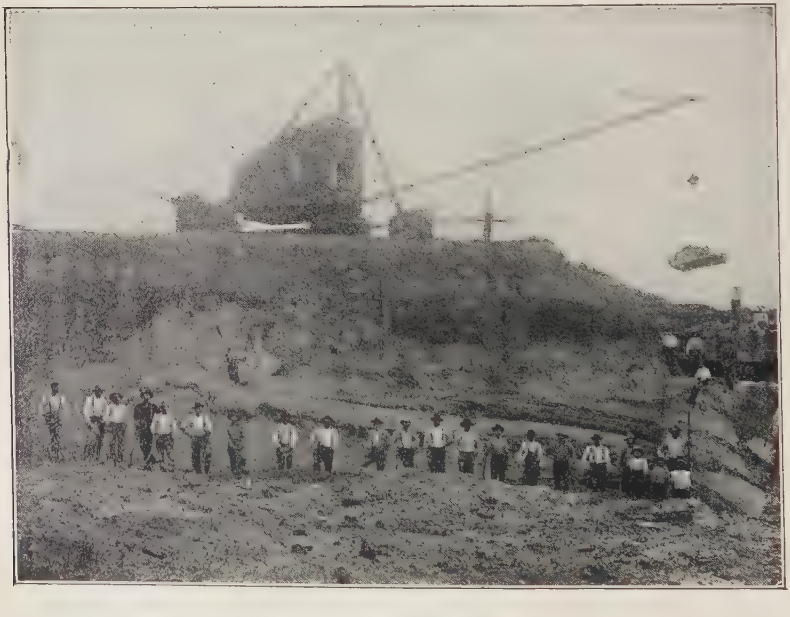

FIG. 132.—Cretaceous stoneware-clay, Red Wing, Minn. (Photo loaned by Red Wing Stoneware Co.)

Uses.—The Decorah shale is used for common brick, pressed brick, hollow ware, fancy brick, and drain-tile. The Cretaceous shales are employed for stoneware and sewer-pipe. The Pleistocene clays for common brick, hollow brick and drain-tile. Many of the Pleistocene clays require careful firing to prevent black coring.

REFERENCES ON MINNESOTA CLAYS

1. Berkey, C. P., Origin and Distribution of Minnesota Clays, Amer. Geol., Vol. XXIX, p. 171, 1902.
2. Grout, F. F., Clays and Shales of Minnesota, U. S. Geol. Surv., Bull. 678, 1918.
3. Grout, F. F., and Soper, E. K., Preliminary Report on the Clays and Shales of Minnesota, Minn. Geol. Surv., Bull. 11, 1914.
4. Winchell, A., County Descriptions in the Series of Final Reports, Vols. I, II, and III of the Minn. Geol. and Nat. Hist. Surv.
5. Winchell, N. H., Brick-clays, Minn. Geol. and Nat. Hist. Surv., Miscel. Pub., No. 8, 1881.

MISSISSIPPI

The clay-bearing formations of Mississippi include the Devonian, Mississippian, Cretaceous, Tertiary and Quaternary, and form perhaps the most important mineral asset of the State. The general distribution of the clay-bearing formations is indicated on the map (Fig. 133). All of these are not of equal importance. Both the Devonian and the Mississippian carry beds of shale, but they do not appear to have been worked.

Of the Cretaceous formations the Tuscaloosa, which occupies a comparatively small area in northeastern Mississippi, is the most valuable. Logan (Ref. 2) states that it carries refractory clays, but the chemical analyses show that most of them are rather high in silica, although they are commonly low in iron oxide. (For tests see Ref. 5.)

The Midway division of the Tertiary found in northeastern Mississippi carries clays which are of medium quality and have been but little used.

In the Wilcox group are found the most valuable clays at present produced in the State. The outcrops extend across the State in a northwesterly direction, but are sometimes covered by later formations. There are three subdivisions which in descending order are the Grenada, Holly Springs and the Ackerman. The Wilcox as a whole consists of beds of clay, sand and lignite, and the series dips gently to the westward. (Refs. 4 and 2.)

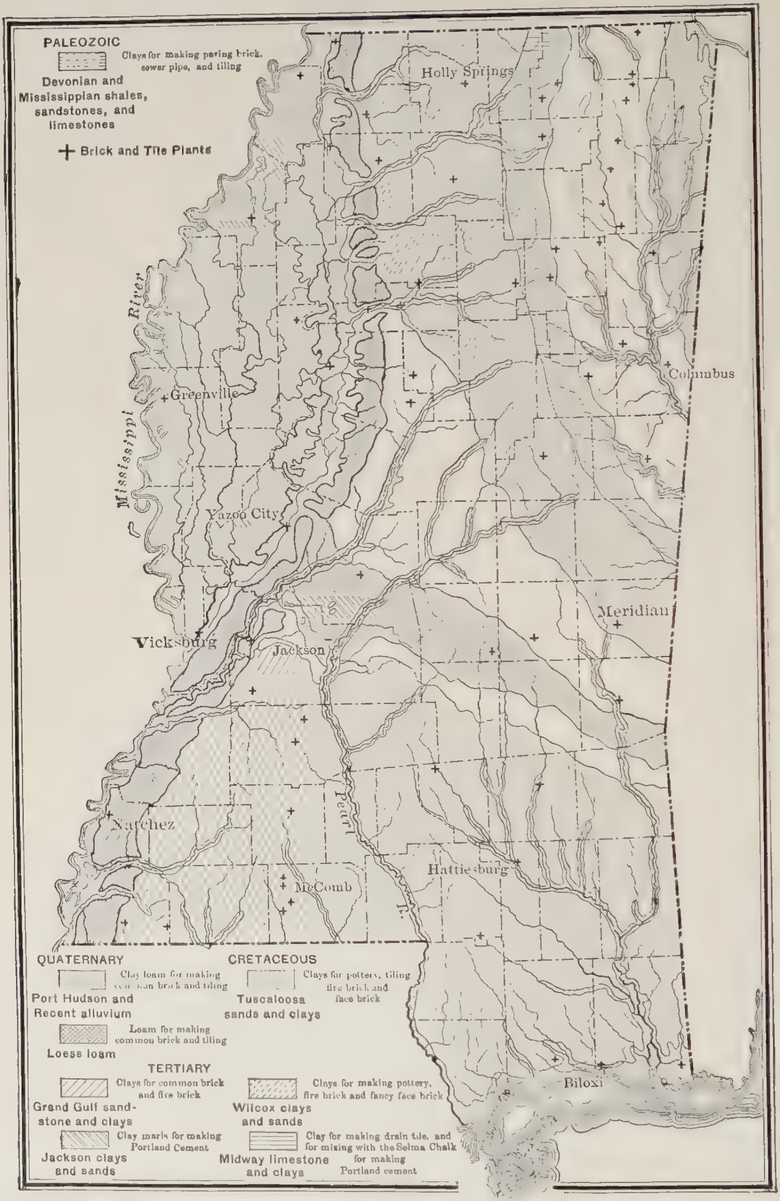
PALEOZOIC
Clays for making paving brick, sewer pipe, and tiling
Devonian and Mississippian shales, sandstones, and limestones
Brick and Tile Plants
Holly Springs
Mississippi River
Greenville
Columbus
Yazoo City
Meridian
Vicksburg
Jackson
Pearl
Natchez
Hattiesburg
McComb
Biloxi
QUATERNARY
Clay loam for making common brick and tiling
Port Hudson and Recent alluvium
Loam for making common brick and tiling
Loess loam
CRETACEOUS
Clays for pottery, tiling fire brick and face brick
Tuscaloosa sands and clays
TERTIARY
Clays for common brick and fire brick
Grand Gulf sandstone and clays
Clays for making pottery, fire brick and fancy face brick
Wilcox clays and sands
Clay marls for making Portland Cement
Jackson clays and sands
Clay for making drain tile, and for mixing with the Selma Chalk for making Portland cement
Midway limestone and clays

FIG. 133.—Map of Mississippi showing the geologic age and distribution of the clay-bearing formations. (After W. N. Logan, Miss. Geol. Surv., Bull. 2.)

The Ackerman carries dark gray lignitic and ferruginous clays and little is known regarding them. The Holly Springs member is prevailingly sandy, but there are lenses of variously colored clays, some of the better ones, as at Holly Springs having been used for stoneware. The Grenada which is well exposed in the northwestern corner of the State as in Tallahatchee County, is of considerable importance as a source of refractory bond clays (Ref. 6), and some of which have been actively worked.

The following physical tests of one will indicate their character (Ref. 6).

Physical Tests of Refractory Bond Clay, Enid, Miss.

Workability: plastic; smooth; works well in molding; dries well.

	Per cent
Water of plasticity	35.20
Volume air shrinkage	30.48
Linear air shrinkage, calculated	11.00

		Pounds per square inch
Modulus of rupture, dried:	Raw clay	533.6
	Mixture, 1 clay : 1 sand	404.5

Firing Tests

Temperature, ° C.	Porosity, per cent	Color	Volume fire shrinkage, per cent	Linear fire shrinkage, per cent
1190	2.5	Light brown	22.80	8.3
1250	2.02	Deep cream	25.49	9.4
1310	2.37	Brown	26.00	9.5
1370	2.00	Buff	25.20	9.3
1410	14.40	Deep buff	Over fired	....

Test made by U. S. Bur. Mines. From Bull. 708, U. S. Geol. Surv.

REFERENCES ON MISSISSIPPI CLAYS

1. Logan, W. N., Brick-clays and Clay Industry of Northern Mississippi, Miss. Geol. Surv., Bull. 2, Pt. I, and Bull. 4, Pt. II, 1904.
2. Logan, W. N., The Pottery Clays of Mississippi, Miss. Geol. Surv., Bull. 6, 1914.
3. Logan, W. N., and Hand, W. F., Preliminary Reports on the Clays of Mississippi, Miss. Geol. Surv., Bull. 3, 1905.
4. Lowe, E. N., Miss. Geol. Surv., Bull. 10, p. 23, 1913.
5. Lowe, E. N., U. S. Geol. Surv., Bull. 708, pp. 206–211, and 249–255, 1922.
6. Ries, H., U. S. Geol. Surv., Bull. 708, p. 239–249, 1922.

Analyses of Mississippi Clays

	I	II	III	IV	V	VI	VII	VIII	IX
Silica (SiO_2)	74.45	71.67	77.57	75.11	71.13	67.72	59.22	60.00	63.35
Alumina (Al_2O_3)	11.62	8.10	7.25	10.70	9.12	10.86	10.30	27.80	13.70
Ferric oxide (Fe_2O_3)	3.38	7.90	6.25	5.50	7.75	5.51	4.70	.75	7.90
Lime (CaO)	1.69	.90	.50	.60	.42	.85	1.68	1.38	.80
Magnesia (MgO)	.94	.94	1.90	.47	.63	.70	1.18	.00	.60
Sulphur trioxide	.43	.62	.17	.....	.08	.54	.23	.20	.34
Loss on ignition	4.23	4.85	3.70	3.20	4.92	8.01	7.00	8.20	6.50
Moisture	2.81	2.15	2.13	1.81	4.95	4.25	10.06	.69	6.02
Total	99.55	97.13	99.47	97.39	99.00	98.44	94.37	99.02	99.21
Clay substance	29.39	20.49	18.34	27.07	23.07	27.47	.....	70.45	34.66
Free silica	60.89	62.15	69.05	62.53	60.41	12.77	.....	17.35	47.24
Impurities	8.44	10.36	8.82	6.57	8.88	7.60	.....	2.33	9.64
Total shrinkage, per cent	6⅔	.....	6⅔	.....	10	8	15	.....	8
Tensile strength, pounds per square inch	115	100	60	72	87	75	187	.....	133
Water required, per cent	19	20	15	18	.....	17	27	.....	16

I. Yazoo alluvium (buckshot clay), Clarksdale.
II. Yazoo alluvium (sandy).
III. Brown loam, Columbia formation, Pontotoc.
IV. Loess, Batesville.
V. "Joint clay," Lafayette formation, Aberdeen.
VI. Brick clay, Jackson formation, Jackson.
VII. Siliceous clay, Claiborne formation, Vaiden.
VIII. Pottery clay, Wilcox formation, Wilcox.
IX. Residual clay from Selma chalk formation, Agricultural College.
Nos. I–IX from Miss. Geol. Surv., Bull. 2, 1907.

MISSOURI

In the variety of its clays Missouri (Ref. 8) stands well up towards the head of the clay-producing States. As can be seen from a glance at the map (Fig. 134), the clay-bearing formations range from Cambrian to Pleistocene, exclusive of Cretaceous, and Jura-Trias.

A discussion of the clays by formations is not perhaps wholly satisfactory, but is better in order to maintain uniformity of treatment as far as possible.

Paleozoic Limestone Clays

These consist of four kinds, namely, kaolins, flint-clays, ball-clays, and stoneware-clays.

Kaolins.—The Missouri kaolins occur south of the Missouri River (Fig. 134) and are separable into three districts. These, together with the formations in which the kaolin occurs, are:

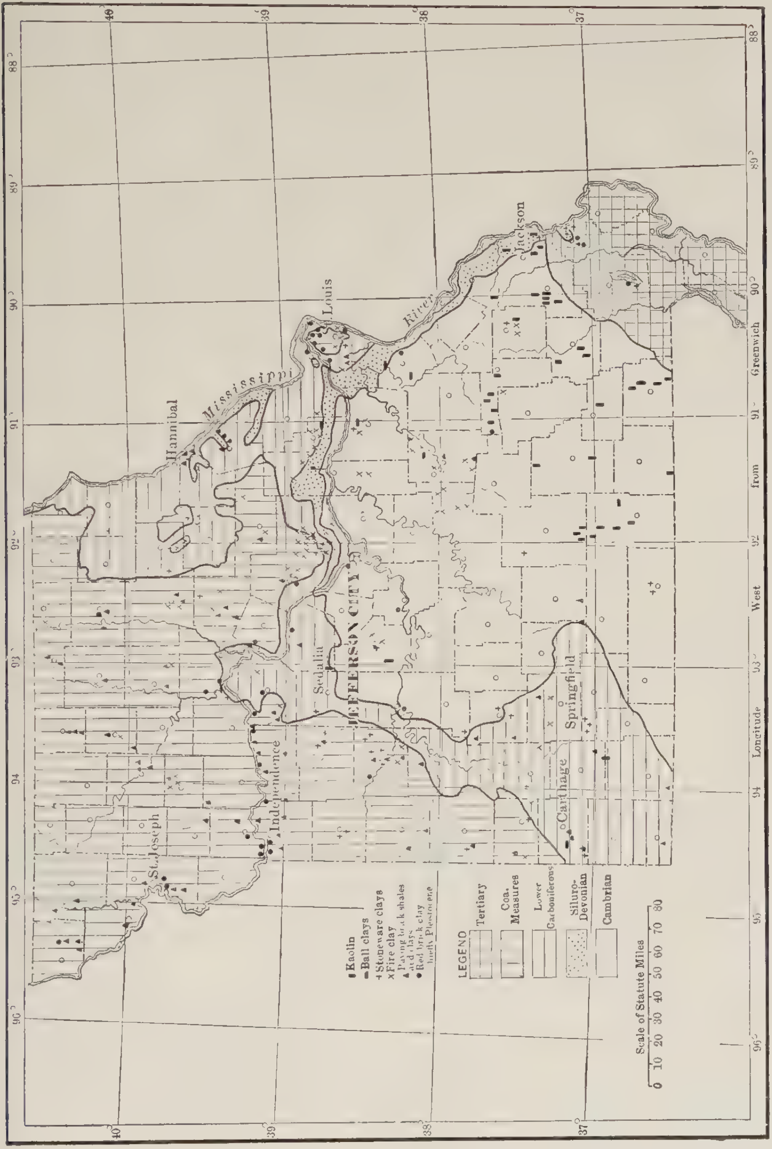

FIG. 134.—Map of Missouri, showing distribution of clay-bearing formations, and location of clay-pits. (Adapted from Wheeler, Mo. Geol. Surv., XI, p. 48, 1896.)

Southeastern district of Cape Girardeau, Bollinger, and Howell counties, in Ordovician and Cambrian limestones.

Central district of Morgan and Cooper counties, in Ordovician limestone.

Southwestern district of Aurora and Lawrence counties, in Mississippian limestone.

According to Wheeler, the kaolins appear to be the insoluble fine residual matter left by the removal by solution of heavy beds of limestone. Only those of the southeastern district have been worked, and these to but a limited extent. The output has been sold for use in the manufacture of white ware, paper, or kalsomine, and Glen Allen is the most important locality.

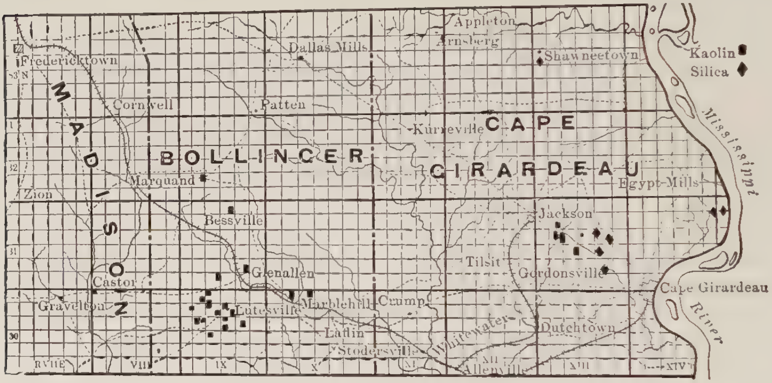

FIG. 135.—Map showing distribution of Missouri kaolins. (After Wheeler, Mo. Geol. Surv., XI, p. 200, 1896.)

HIGH ALUMINA FLINT CLAYS

Wheeler (Ref. 8) in 1897 called attention to a remarkable series of flint-clay deposits found chiefly in central Missouri (Fig. 136). The deposits are usually basin shaped (Fig. 137) and occupy depressions in the Paleozoic rocks. In Crawford and Gasconade counties they appear to be in Pennsylvanian sandstones, but Wheeler refers to others which are in limestone. While some of the deposits show only a fine-grained flint-clay of typical character in others the flint-clay may have oolitic bodies scattered sparingly through it or grade into a phase which is largely oolitic. These oolites are made up of the mineral diaspore, and consequently when present in great quantity the clay runs very high in alumina. Indeed these diaspore clays have become the basis of a rather important local clay-mining industry.

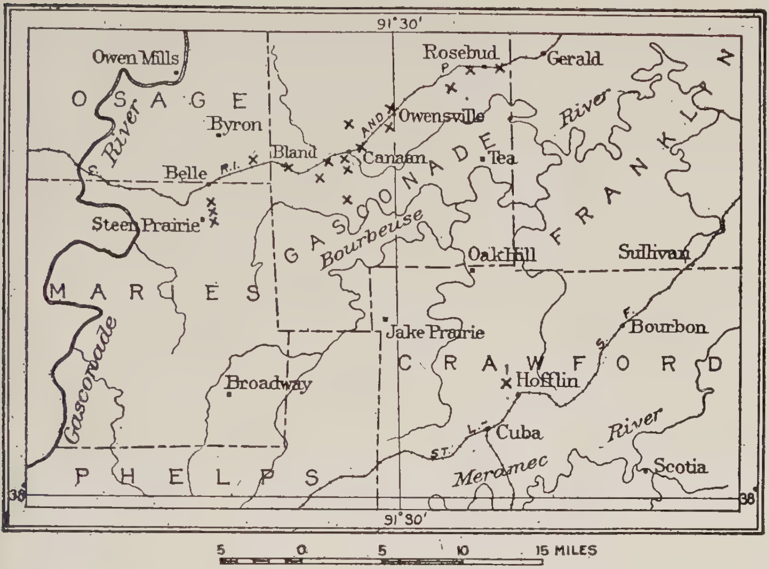

Fig. 136.—Map showing flint clay area of central Missouri, and location of pits ×. (U. S. G. S., Bull. 708, 1922.)

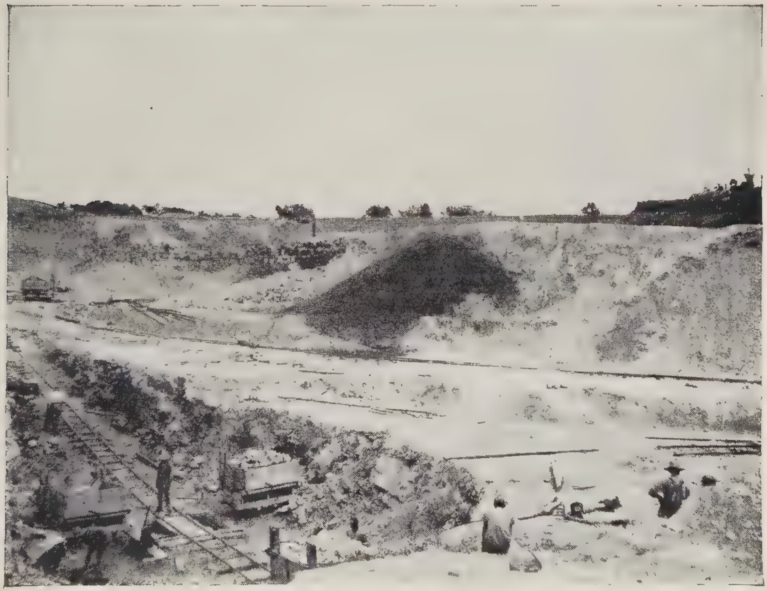

Fig. 137.—Pit in flint and diaspore clay district near Owensville, Mo. (H. Ries, photo.)

The following partial analyses were supplied by M. H. Thornberry of the University of Missouri:

	I	II	III	IV	V	VI	VII
SiO_2..........	11.50	18.84	10.15	6.24	3.60	1.68	13.54
Al_2O_3.........	74.03	62.69	72.87	68.02	81.68	68.96	71.83
Fe_2O_3.........	.97	1.21	.84	12.48	1.32	9.28	1.21
Ignition.......	13.20	13.77	14.95	13.10	13.72	13.77	12.71

The diaspore clay is of value in the manufacture of refractory products.

Stoneware-clays.—These have a similar origin to the flint-clays, but are less pure and have not been consolidated by secondary chemical changes. They are of local extent, and are found in rocks ranging from the Lower Carboniferous down to the Cambrian, but the Burlington and Trenton limestones appear to be the most favorable situations.

COAL-MEASURES

The Coal-measures of Missouri contain two important series of deposits, namely, plastic fire-clays and impure shales.

Plastic fire-clays.—All of the Missouri plastic fire-clays occur in the Carboniferous, at the base of the Coal-measures, and are found in the eastern part of the State in two different basins known respectively as the St. Louis and Mexico areas. The former is on the western edge of the eastern interior coal-field, and the latter on the eastern edge of the western interior field.

In the St. Louis basin there are several beds of clay and shale, but only the St. Louis fire-clay seam is refractory. This has an average thickness of 6 to 8 feet, with a sandstone floor, a thin bituminous coal-roof, and is worked by shafts or adits. It is hard when fresh, but disintegrates on exposure.

A special grade known as pot-clay comes from a purer and more uniform seam near the middle or top of the bed.

The St. Louis clay is coarse-grained, often carries pyrite, and although high in iron, still the latter is uniformly distributed and finely divided. The range of physical properties of this clay is given by Wheeler as follows: average tensile strength, 80 to 150 lbs. per square in.; air-shrinkage, 6 to 9 per cent; fire-shrinkage, 4 to 8.5 per cent; vitrification at 2300° to 2450° F.; viscosity, 2500° to 2700° F. This clay is much used for glass pots, zinc-retorts, and gas-retorts. It also makes a durable

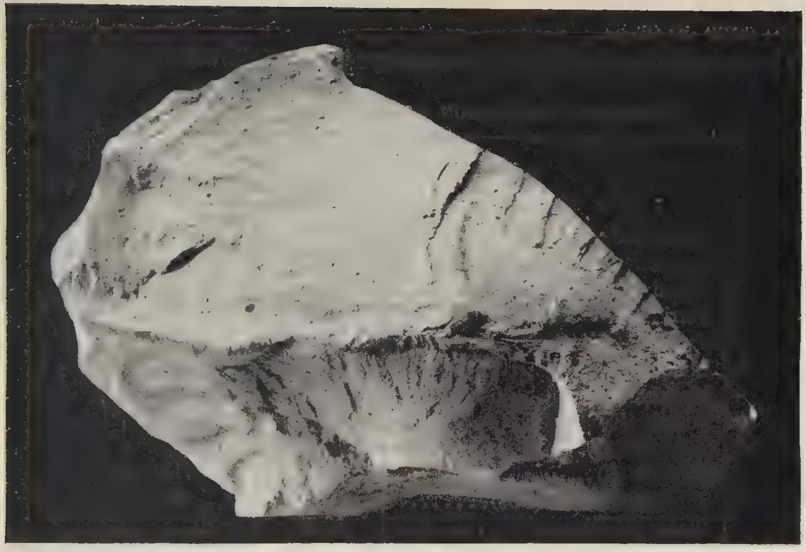

FIG. 138.—Flint clay, from Missouri.

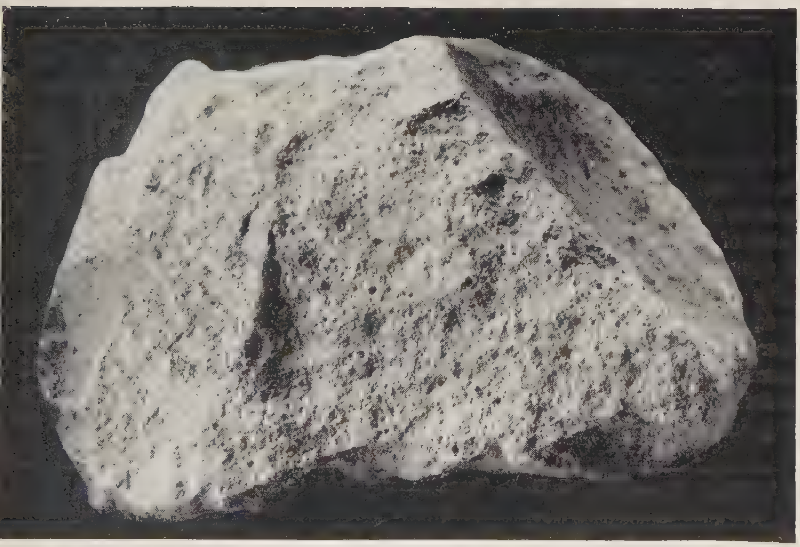

FIG. 139.—Diaspore clay from Missouri. Note the oolites.

fire-brick if not exposed to excessive heat, as its fusion-point does not exceed cone 30 or 31.

The average composition of seven clays was as follows:

AVERAGE COMPOSITION OF ST. LOUIS FIRE-CLAY

	Mine-run	Washed
Combined silica (SiO_2)	32	32
Free silica (SiO_2)	30	25
Alumina (Al_2O_3)	24	24
Ferric oxide (Fe_2O_3)	1.9	1.85
Ferrous oxide (FeO)	1.2	1.00
Lime (CaO)	.7	.7
Magnesia (MgO)	.3	.2
Potash (K_2O)	.5	.55
Soda (Na_2O)	.2	.10
Sulphur (S)	.3	.18
Sulphur trioxide (SO_3)	.35	.40
Water (H_2O)	10.5	10
Moisture	2.7	3
Total fluxes	5.5	4.8

The Mexico clay includes one bed which is worked at Fulton, Mexico, and Vandalia. It ranges from 6 to 40 feet in thickness, but only the

PHYSICAL TEST OF CHELTENHAM FIRE-CLAY, ST. LOUIS, MO.

	I	II	III	IV	V
Water of plasticity	31.14	43.63	34.66	29.54	25.52
Volume air shrinkage	38.42	43.63	42.63	37.02	28.52
Modulus of rupture, dried clay, pounds per square inch	838	328	990	575	489
Modulus of rupture, clay 1 : sand 1, pounds per square inch	399	351	554	351	263
Temperature vitrification, ° C	1290	1200	1200	....	1400
Temperature overfiring, ° C	1320	1430	1320	1320	1425
Cone, softening point	27	32	27	....	31
Slaking time, minutes	52	33	117	26	46

Bleininger, A. V. and Loomis, G. A., Trans. Amer. Ceram. Soc., Vol. XIX, p. 601, 1917.

I. Not a high-grade bond clay.
II. Promising as a crucible material.
III. Not suitable for steel-melting crucibles or glass refractories. Should be useful for brass-melting work.
IV. Good plasticity, dries well.
V. Good plasticity, dries well. Somewhat deficient in bonding power.

lower 6 to 12 feet are worked, and this through shafts. The range of physical properties is given by Wheeler as follows: Average tensile strength, 40 to 80 lbs. per square inch; air-shrinkage, 4 to 5 per cent; fire-shrinkage, 6 to 7 per cent; vitrification, 2400° to 2500° F.; viscosity, 2600° to 2700° F. The average composition is also given by Wheeler as follows:

Silica (SiO_2)	52.00
Alumina (Al_2O_3)	33.00
Ferric oxide (Fe_2O_3)	1.5
Lime (CaO)	.5
Magnesia (MgO)	.7
Alkalies (Na_2O,K_2O)	12.00
Total fluxes	3.4

Stoneware-clays.—Those found in the coal-measures are the most important known in the State, including many clay- and shale-beds, the most extensive of which are found in Henry County. They have been much used by potteries in Kansas as well as other portions of the West and Southwest. The so-called fire-clays of the barren coal-measures are usually impure, and consequently fusible and likely to blister or give a dark body after burning. The true fire-clays have also been used to some extent for stoneware.

Impure shales.—Many excellent beds of these are found in the coal-measures. They are all impure, but are eminently useful for making paving-brick, sewer-pipe, drain-tile, roofing-tile, terra-cotta, brick and hollow ware, but they are not usually pure enough for refractory goods, stoneware, or white ware, and their main use has been for paving-bricks. Nearly all of them make a fair grade of brick by any process of molding, but the majority have to be finely ground or weathered.

In their physical properties the range is: average tensile strength, 50 to 250 lbs. per square inch, usually between 125 and 175 lbs.; water required for tempering, 16 to 25 per cent; air-shrinkage, 4 to 8 per cent; fire-shrinkage, 1 to 10.6 per cent, but usually 4 to 6 per cent; incipient fusion, 1500° to 1700° F.; vitrification, 1700° to 1900° F.

The range of chemical composition is given by Wheeler as:

Silica (SiO_2)	50–75
Alumina (Al_2O_3)	10–27
Ferric oxide (Fe_2O_3)	3–10
Lime (CaO)	.5–2
Magnesia (MgO)	.5–2
Alkalies (Na_2O, K_2O)	3–4
Water (H_2O)	5–12
Total fluxes	10–15

TERTIARY

The Tertiary beds occupy a small area in the southeastern corner of the State. Some of the deposits now worked in Butler county showed a thickness of 59 and 80 feet. The clays contain disseminated lignite, and dolomite concretions; they are used as a bond for abrasive wheels, in floor, wall and decorative tile, in electrical porcelain and sanitary ware. The iron stained upper clay is used in saggers.[1]

PLEISTOCENE

Pleistocene clays are widely scattered over the State, and form the main supply of material for common brick, although a few are sufficiently pure and plastic for stoneware manufacture.

Three types are recognizable:

1. **Loess-clays,** confined mostly to the neighborhood of the larger streams, especially the Missouri and Mississippi. They are yellow to brown in color, unstratified, and often of columnar structure. Their thickness is considerable, 75 to 100 feet being common along the lower Missouri, while at the Iowa line they have a thickness of 200 feet. The loess extends from 3 to 10 miles back from the streams, and appears to get stronger as the distance from the rivers increases, this change interfering with its being worked by the mud process. It is, however, the most valuable of the surface-clays.

2. **Glacial clays,** of varying character, confined to the counties north of the Missouri River, and rarely over 50 feet thick. The material is usually very strong, red-burning, and often contains bowlders or concretions, but occasionally shows beds of better clay suitable for stoneware or drain-tile.

3. **Alluvial clays**, found along the present streams, and of little importance.

The tables on pp. 479, 480 give the analyses and physical tests of a number of Missouri clays which may be regarded as representative.[2]

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[1] Buehler, H. A., Ceramic Age, IX, p. 50, 1927.

[2] These were selected for the writer by Prof. H. A. Wheeler.

Analyses of Missouri Clays

ULTIMATE ANALYSES

	I	II	III	IV	V	VI	VII	VIII
Silica (SiO_2)	55.12	72.30	54.90	74.39	43.82	71.94	54.80	72.00
Alumina (Al_2O_3)	30.71	18.94	18.03	12.03	38.24	17.60	23.73	11.97
Ferric oxide (Fe_2O_3)	1.51	0.40	6.03	4.06	0.23	2.35	8.67	3.51
Lime (CaO)	0.54	0.68	2.88	1.50	1.93	0.62	0.64	1.80
Magnesia (MgO)	trace	0.39	1.10	1.52	......	0.56	2.23	1.35
Potash (K_2O) Soda (Na_2O)	1.37	0.42	3.40	3.01	0.73	1.51	3.80	3.25
Moisture	......	......	6.72	......	......	1.01	......	......
Comb. water	10.56	7.04	6.90	3.17	14.94	5.27	6.00	6.42

	IX	X	XI	XII	XIII	XIV	XV
Silica (SiO_2)	49.04	65.01	61.19	59.36	60.70	73.92	43.56
Alumina (Al_2O_3)	34.85	19.30	15.48	23.26	18.22	11.65	41.48
Ferric oxide (Fe_2O_3)	0.71	4.91	5.49	3.06	7.58	4.74	0.35
Lime (CaO)	1.33	1.40	1.95	0.65	2.68	1.45	0.45
Magnesia (MgO)	1.04	0.40	1.56	0.42	trace	0.60	......
Potash (K_2O) Soda (Na_2O)	0.85	2.60	2.82	0.63	3.67	3.13	0.20
Titanic oxide (TiO_2)	......	......	......	1.01	......	......	......
Sulphur trioxide (SO_3)	......	......	......	0.35	......	......	......
Moisture	......	1.03	3.11	2.74	......	2.18	......
Comb. water	12.33	5.51	9.02	10.20	7.77	3.08	14.05

Physical Tests of Missouri Clays

	I	II	III	IV	V	VI	VII	VIII
Size of grain*	C.	V.F.	V.F.	C.	V.F.	V.F.	V.F.	F.
Average tensile strength, pounds per square inch	62	12	380	131	8	150	115	151
Per cent H_2O for plasticity	14.8	23.2	22.3	17.2	15.1	16.5	21.5	18.4
Plasticity	lean	lean	very plastic	lean	very lean	plastic	plastic	lead
Air-shrinkage, per cent	4.4	4.0	9.6	5.7	3.1	5.5	5.9	5.1
Fire-shrinkage, per cent	6.4	8.4	1.4	4.3	11.6	2.2	2.8	5.7
Speed*	R.	S.	S.	R.	S.	S.	V.S.	R.
Incipient fusion, ° F.	2200	2200	1600	2000	2350	2100	1500	2000
Complete fusion, ° F.	2400	2500	1750	2000	2700	2300	1700	2200
Viscosity, ° F.	2600	......	1900	2300	2700	2500	1900	2200
Specific gravity	2.46	1.89	2.01	2.09	2.85	2.34	2.37	2.17

* C. = coarse; V.F. = very fine; F = fine; S. = Slow; R. = rapid; V.S. = very slow.

PHYSICAL TESTS OF MISSOURI CLAYS *(continued)*

	IX	X	XI	XII	XIII	XIV	XV
Size of grain	V.F.	C.	V.F.	C.	C.	C.	F.
Average tensile strength, pounds per square inch	198	92	273	78	177	173	13
Per cent H_2O for plasticity	23.4	18.4	23.1	15.0	20	17.1	15.2
Plasticity	plastic	slightly lean	very plastic	lean	plastic	plastic	very lean
Air-shrinkage, per cent	7.7	5.2	8.0	6.3	5.3	5.3	2.4
Fire-shrinkage, per cent	9.8	3.5	1.5	5.4	8.3	5.5	8.9
Speed*	S.	R.	V.S.	R.	R.	R.	S.
Incipient fusion, ° F.	1800	1850	1650	2250	1700	1800	2400
Complete fusion, ° F.	2100	2050	1800	2450	1900	1950	2700
Viscosity, ° F.	2400	2250	1950	2650	2100	2050	2750
Specific gravity	1.69	2.41	2.05	2.41	....	1.98	2.39

* C. = coarse; V.F. = very fine; F. = fine; S. = slow; R. = rapid; V.S. = very slow.

LOCALITIES OF THE PRECEDING

No.	Locality	Geological age	Uses
I	Mexico	Coal-measures	Fire-brick
II	Glen Allen	Residual	White ware
III	Norborne	Pleistocene	Railway ballast
IV	Jefferson City	Coal-measures	Red brick
V	Leasburg	....	Fire-brick
VI	Calhoun	Coal-measures	Stoneware
VII	Kansas City	Coal-measures	Paving-brick
VIII	Kansas City	Coal-measures	Red brick
IX	De Soto	Residual	White ware
X	Moberly	Coal-measures	Paving-brick
XI	St. Peter's	Pleistocene	Railway ballast
XII	St. Louis (Evens and Howard)	Coal-measures	Fire-brick
XIII	Prospect Hill, St. Louis	Coal-measures	Roofing-tile
XIV	St. Louis (Hyd. Br. Co.)	Coal-measures	Red-brick
XV	Truesdale (Kelley's pit)	Coal-measures	Fire-brick

REFERENCES ON MISSOURI CLAYS

1. Buehler, H. A., Biennial Reports of the State Geologist, from 1909 to date.
2. Fenneman, N. M., Geology and Mineral Resources of the St. Louis Quadrangle, U. S. Geol. Surv., Bull. 438, 1911.
3. Galpin, S. L., Studies of Flint Clays and Their Associates, Trans. Amer. Ceram. Soc., Vol XIV, p. 301–46, 1912.
4. Orton, E., Jr., The Kaolin Deposits of Bollinger County, Mo., Trans. Amer. Ceram. Soc., Vol. IX, p. 62–94, 1907.
5. Ries, H., Diaspore Clays, U. S. Geol. Surv., Bull. 708, p. 135, 1922.
6. Seamon, W. H., Zinciferous Clays of Southwest Missouri, Amer. Jour. Sci., Jan., p. 38, 1890.
7. Thornberry, M. H., A Treatise on Missouri Clays, Issued by School of Mines and Metallurgy, Rolla, Mo., 1925.
8. Wheeler, H. A., Clay Deposits, Mo. Bur. Geol. and Mines, Vol. XI, 1896. A most comprehensive report.
9. Wysor, D. C., Diaspore Clay of Arkansas and Missouri, Jour. Amer. Ceram. Soc., Vol. II, p. 501, 1923.

MONTANA

Montana has never assumed prominence as a producer of clay products, and there is but little published information on the clays of that State, although the presence of good ones will no doubt be demonstrated when the demand for them develops.

Common brick-clays are known to occur in many parts of the State, but the only fire-clay district of importance which has been developed is that lying in the eastern part of Cascade County.

In this region the Kootenai formation of the lower Cretaceous is known to carry important deposits of refractory clay, which have been worked at Belt and Armington, small coal-mining towns lying in the northwestern part of the area.

The section of the Kootenai formation in this area shows about 450 feet of sandstones and shales. Near the center of the section is a bed of fire-clay which was formerly mined, while about 100 feet above the base of the section is a bed of plastic clay, which is now extracted in considerable quantities. Although the clay is found at a number of points, it does not represent a continuous deposit. Moreover, the beds, while appearing horizontal to the casual observer, are bent into a series of very gentle folds and also broken in places by small faults, having a throw of from 5 to 15 feet.

The plastic clay is shipped to Anaconda where it is used for the manufacture of fire-bricks to supply the large smelters at that locality.

The following analyses, given by Fisher, represent the composition of the plastic fire-clay:

Analyses of Fire Clays from Belt Region, Montana

	I	II
Silica (SiO_2)	55.38	53.70
Alumina (Al_2O_3)	30.86	27.20
Ferrous oxide (FeO)	0.86	....
Ferric oxide (Fe_2O_3)	....	5.00
Lime (CaO)	0.40	tr.
Magnesia (MgO)	1.03	tr.
Ferric sulphide (FeS_2)	2.23	....
Soda (Na_2O)	0.26	....
Potash (K_2O)	1.04	2.90
Sulphur trioxide (SO_3)	....	0.30
Moisture	0.84	....
Ignition loss	6.86	10.00
Total	99.82	99.10

I. Analysis of clay worked by Anaconda Copper Mining Co. at Arlington, and sampled by C. A. Fisher.
II. Analysis of clay from same district supplied by Anaconda reduction works.

REFERENCES ON MONTANA CLAYS

1. Fisher, C. A., Clays in the Kootenai Formation near Belt, Montana, U. S. Geol. Surv., Bull. 340, 1908.

NEBRASKA

According to E. H. Barbour (Ref. 1), this State contains an abundance of clays, the most important being found in the Carboniferous and Dakota Cretaceous formations, while others occur in the Tertiary and Quaternary.

Carboniferous

The rocks of this formation (Ref. 2) occupy a V-shaped area in southeastern Nebraska, with the apex in the vicinity of Blair, and the base along the Kansas-Nebraska line from a point near Wymore to the Missouri River. The Carboniferous, including the Permian, consists of massive grayish-yellow limestones, interstratified with clays, shales, and an occasional layer of coal. " The clays are usually of a dull-blue color interbedded with streaks of red and buff-colored sands, but there are also thin layers of disintegrated limestone, calcite concretions, and sand. . . .

" Frequently these thick deposits of clay form prominent bluffs along either side of the valley for some distance, especially where the clay is protected from erosion by some overlying layer of a somewhat harder material, such as limestone. . . . There are also many other available clay-banks along the Platte and Missouri rivers, notably at Nebraska City, where extensive brick-works are in operation, utilizing the clays of the Carboniferous for vitrified paving-brick. Terra-cotta ware has also been made here. Other localities where the clays are well exposed, and in some cases worked, are Minorsville, Peru, and Table Rock." Nearly all of the best deposits along the Missouri River in southeastern Nebraska are located along the Nebraska City branch of the Burlington and Missouri Railroad.

CRETACEOUS

The Dakota formation rests stratigraphically on top of the Carboniferous, with an unconformity between. The surface underlain by it is on the west and northwestern sides of the Carboniferous area, forming a strip about 30 miles wide and 200 miles long. It also forms a belt along the Missouri River north of the Carboniferous area. The formation consists of a series of shales and sandstones, but the latter, owing to their higher resistance to erosion, stand out more prominently, so that the mellowed outcrops of the shales are less noticeable. These shales vary from a sandy material of yellowish-brown color to highly plastic clays, the different beds showing a great variety of colors. Lens-shaped layers of sandstone are, however, not uncommon in the shale. These Dakota clays are available at many localities, and are said to have given excellent results for both pottery and brick manufacture.

The Graneros shale is not used, but the Carlile shale is worked at Superior for Portland cement manufacture. The Pierre shale underlies a large area in the western part of the State, but is mostly covered by Tertiary and Quaternary deposits. No use is made of it.

LOESS AND ALLUVIUM

The great bulk of brick made in Nebraska are manufactured from loess and alluvium (Ref. 3). The loess, or "bluff-deposit," as it is commonly called, consists of a light buff-colored loam, of generally uniform texture, but containing some shells. It is found over about half the area of the State.

Glacial drift clay is used at a few localities for making common brick, and has sometimes been mixed with the loess.

The alluvium or valley-wash is a dark-colored soil of very fine texture, with interbedded layers of fine sand and gravel, and is being deposited at the present time in narrow strips along nearly all the large streams in the State. This alluvial clay is sometimes used for making common red brick.

REFERENCES ON NEBRASKA CLAYS

1. Barbour, E. H., Preliminary Report of the Clay Industry of Nebraska, Nebr. Geol. Surv., Vol. IV, p. 441–493, 1917.
2. Gould, C. N., and Fisher, C. A., Ann. Rept. Neb. State Board of Agric. for 1900, p. 185.
3. Fisher, C. A., Ann. Rept. Neb. State Board of Agric. for 1900, p. 181.

NEVADA

Nevada is of little importance as a clay-producing State, and what little information has been published relates chiefly to isolated deposits of a unique character.

White-burning refractory clays have been reported from several localities in Nevada, but there has been no steady production of this class of material.

Near Oreana there is said to be a large deposit of white gritty kaolin which occurs as a fault gouge in rhyolite. About 25 miles east southeast of Lovelocks there is a sedimentary deposit of hard, white, gritty clay 75–100 feet thick. It apparently belongs to the Paleozoic series, but some of its properties may be due to weathering (Ref. 1).

Near Beatty, Nev. (Ref. 2), there is a peculiar clay which resembles bentonite in that it swells when placed in water and is said to contain a large amount of colloidal material, but mixed with this there is also some hard, gritty substance. In composition it resembles hydrated feldspar with small amounts of impurities. Tests indicate that it may be used in bodies, glazes, and enamels. There is no reliable information as to its extent and geologic occurrence, but it is said to occur in six vertical veins 6–10 feet thick.

REFERENCES ON NEVADA CLAYS

1. Buwalda, J. P., U. S. Geol. Surv., Bull. 708, p. 121–126, 1921.
2. Cox, P. E., and Moulton, D. A., A New Raw Material for Ceramic Uses, Jour. Amer. Ceram. Soc., Vol. VI, p. 937–939, 1923.

NEW JERSEY

Nearly all of the larger geological formations in the State contain deposits of clay, but the important ones belong to the following: Ordovician, Triassic, Lower Cretaceous, Upper Cretaceous, Miocene and Pliocene of Tertiary and Pleistocene.

CAMBRIAN AND ORDOVICIAN

The Cambrian and Ordovician rocks include beds of limestones and shales with some beds of sandstone and quartzite, and occur chiefly in Warren and Sussex counties in the great Kittatinny Valley, but are found also at a few other localities. Southwest of the terminal moraine (Fig. 140) the limestone yields a sticky yellow residual clay with flints, and that worked near Beattystown is of this character. The shale, also, where found south of the moraine is often deeply weathered, and at Port Murray is utilized for the manufacture of fireproofing. There it is found to be red-burning, of low plasticity, and fusing about cone 1.

TRIASSIC

The Triassic or Newark series consists chiefly of red shales and sandstones with masses of trap-rock, and forms a belt extending across the State between the Highlands on the northwest and Cretaceous on the southeast. In places the shale has disintegrated to a sandy clay-soil, which has been used locally for common brick, but the fresh shale has in most cases been found too sandy to make into clay-products, although at one point, Kingsland, the shales have been used with apparent success. They burn to a hard red brick, but fuse at a low cone, and are not highly plastic.

CRETACEOUS

The New Jersey Cretaceous is divisible into three parts, which, beginning at the bottom, are: 1. Clay series of Lower Cretaceous; 2. Clay-marl series of Upper Cretaceous; and 3. Glauconitic marl series (see Fig. 140). Of these three, the first contains many important clay-deposits, the second some clays of economic value, but the third is of no interest in the present discussion.

Lower Cretaceous clay series.—This was termed the Raritan or Plastic Clay series by Dr. Cook (1878) and consists of a number of beds of clay, sand, and even gravel. The clays show great variety, ranging from nearly white or steel-blue fire-clay of high quality to black sandy clays containing varying amounts of pyrite, and useful only for common-brick manufacture. A similar variation is found in the sand-beds. A peculiar feature of the Raritan series is the rapid alternation of strata, so that the clays often change suddenly, both vertically and horizontally, much as shown in Fig. 5. This fact often makes it uncertain whether two pits sunk within a short distance of each other will yield the same kinds of clay.

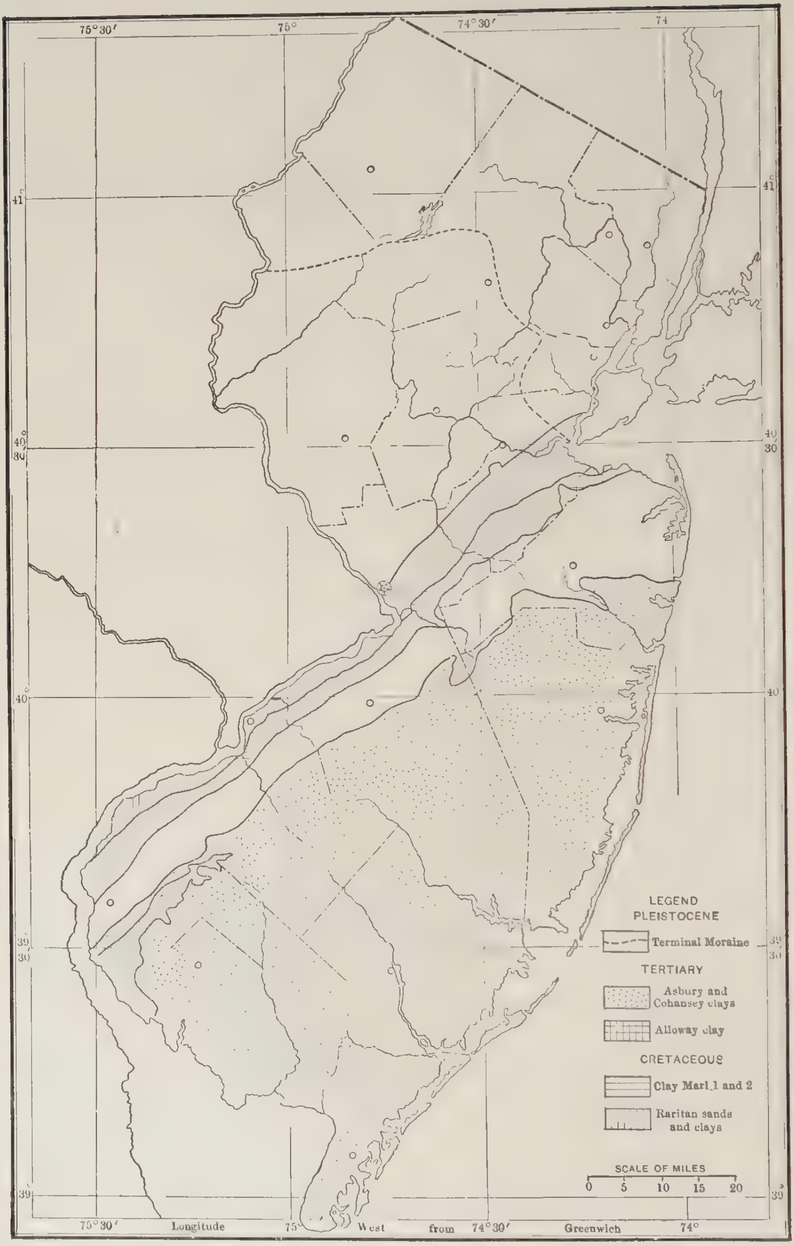


FIG. 140.—Map of New Jersey showing distribution of important clay-bearing formations. (Adapted from map by Kümmel and Knapp, N. J. Geol. Surv., Fin. Report, VI, 1904.)

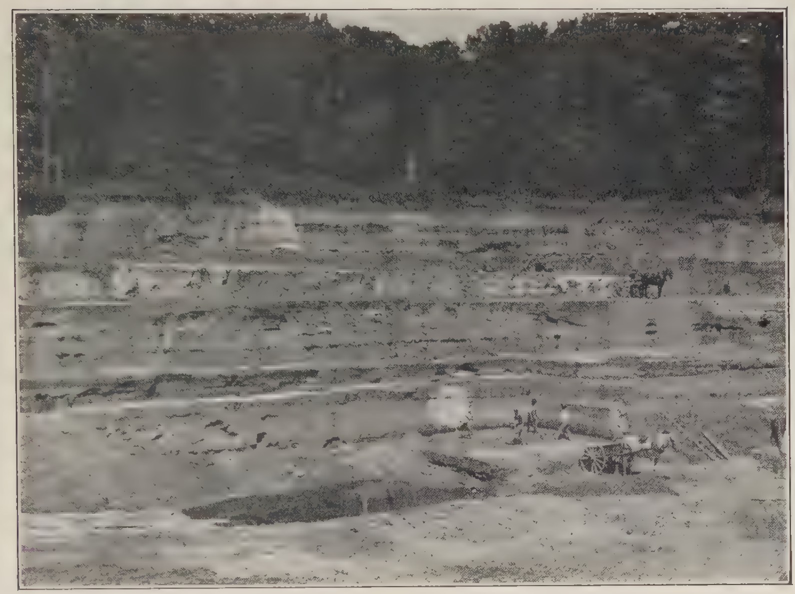


FIG. 141.—Pit of Raritan (Cretaceous) clay, Woodbridge, N. J. (After H. Ries, N. J. Geol. Surv., Fin. Rept., VI, p. 340, 1904.)

FIG. 142.—Clay-loam deposit of shallow character, west of Mount Holly, N. J. (After H. Ries, N. J. Geol. Surv., Fin. Rept., VI, p. 122, 1904.)

Notwithstanding these frequent changes in character and the impossibility of establishing divisions in the Raritan series which can be accurately identified at widely separated intervals, it is possible, nevertheless, to recognize certain divisions, whose general features are sufficiently persistent to permit their being traced throughout the region of Middlesex County in which the beds have been so extensively worked. In other areas these subdivisions do not seem to hold.

The boundary between the upper part of the Raritan clays and the overlying clay marls is easily recognized, the upper bed of the former being a loose sand or sandy clay, while the lower bed of the latter is a glauconitic clay, black when fresh, but rusty brown when weathered, and often fossiliferous. Underlying the Raritan beds is the Triassic shale.

The Raritan series occupies a broad belt (Fig. 140) extending from Raritan Bay across the State to Trenton and Bordentown, and a much narrower strip along the Delaware River to Salem County. Over most of its outcrop across the State it is covered by later formations.

In the Middlesex County area the Raritan is divisible into nine members, which, beginning at the bottom together with their characters, are as follows:

1. Raritan clays. This member carries both a fire-clay and potter's clay. The former is usually drab, but sometimes mottled or black, and generally quite sandy. It is dug around Sand Hills, and sparingly at Woodbridge and Mill Brook. Its main use is for fire-brick, and its refractoriness is usually about cone 27. The potter's clay is a white or bluish-white clay of variable color and composition. It is worked east of Martin's Dock and south of Metuchen.

2. No. 1 fire-sand, a bed of quartz-sand.

3. Woodbridge clays. This, the most important member of the Raritan series, consists of an upper bed of black, laminated sandy clay, and a lower bed of fire-clay. The laminated clay is red-burning, plastic, and contains more or less lignite and pyrite; it is extensively worked for the manufacture of fireproofing, common brick, conduits, etc., and large pits have been opened in it around South River, Sayreville, and other points.

The fire-clay ranges from a fine-grained clay of high plasticity and high refractoriness (cone 35) to sandy clays of lower grade fusing at cone 27. It can be stated in general that the bed is less refractory at the southwest end. This clay is used in the manufacture of fire-brick, pressed brick, retorts, stoneware, and as an ingredient in fireproofing and conduits. A small amount dug near Woodbridge is sufficiently white-burning and refractory for white-ware manufacture.

4. No. 2 sand. Included in this sand formation are two important beds whose names are somewhat misleading, namely, the feldspar and kaolin beds. The *feldspar* is a coarse feldspathic sand or gravel with more or less decomposed feldspar and pellets of white clay, while the *kaolin* is not in any sense such, but is a micaceous quartz-sand.

5. South Amboy fire-clay. This outcrops chiefly south of the Raritan River between Sayreville and South Amboy, but is also found at several points north of it. It is generally a white, light blue, or red-mottled clay, ranging from 15 to 30 feet in thickness, and varying greatly in its quality. Its refractoriness is moderate.

6. No. 3 sand.

7. Amboy stoneware-clay. An important bed of stoneware-clay, best exposed southeast of South Amboy. Like the other members it is of variable character, but the better grades are used for stoneware.

8. Laminated sands of little value.

9. Cliffwood lignitic sands and clays. These form a series of beds of massive black clay and gray-black laminated sands and clays, which often carry lignite and pyrite. They are extensively exposed in the brick-pits around Cliffwood and along Cheesequake Creek, and are all red-burning.

The other Raritan areas, around Trenton, Burlington, Bordentown, Bridgeboro, etc., afford clays of refractory character, but it is not possible to correlate the sections with those of Middlesex County. The Raritan formation is by far the most important clay-bearing formation in New Jersey, containing as it does such a wide range of materials. Even a hasty consideration of the uses to which they are put indicates in a measure what a wide range of materials must be contained within the limits of the Raritan strata, for among the products made from these clays are common brick, fireproofing, drain-tile, conduits, terra-cotta, front brick, fire-brick, stoneware, earthenware, tubs, and sinks, foundry materials, paper filling, etc. The physical tests and chemical analyses on pp. 492 and 493 will serve to give a good idea of their character.

Clay-marl series.—The outcrops of this series extend from the shores of Raritan Bay across the State in a southwest direction to the Delaware River north of Salem, forming a belt varying in width from 2½ to 8 miles. Its base is marked by a glauconitic sandy clay which weathers to a characteristic cinnamon-brown, indurated earth. The top is emphasized by the passage of a bed of loose reddish sand with quartz grains of pea size into a compact greenish marl. At many points a fossil bed 1 to 4 feet thick is present. Five members are recognizable as follows:

1. Black, sandy, often glauconitic clay, weathering cinnamon-brown.
2. Black, non-glauconitic clay, weathering to chocolate.
3. Varicolored sands.
4. Black laminated sand and clay, strongly glauconitic to the southwest.
5. Red quartz-sand. Top.

Both Nos. 1 and 2 are important sources of brick- and sometimes tile-clay, the former being worked near Camden, Keyport, Hightstown, etc., and the latter near Matawan, Kinkora, Maple Shade, Camden, etc. Indeed, the two are sometimes worked in the same or adjoining banks.

TERTIARY

The Tertiary clay-deposits occur in scattered areas lying to the southeast of the Lower Cretaceous belt. They are beds of irregular form, with a tendency towards basin-shaped structure. Owing to the almos universal mantle of sand over this region and the flatness of the surfac prospecting for the deposits is rendered more or less difficult.

The clay-deposits recognized in the recent work of the New Jersey Geological Survey are the Cohansey, Alloway, and Asbury clays. The Cohansey is really a sand formation, but carries many lenses of clay which average 8 to 10 feet in thickness. They occur in the southern portion of the State, in Ocean and Atlantic counties, in southern Burlington, Camden, and Gloucester counties, and in central Cumberland counties. Deposits have been worked at Rosenhayn, Millville, May's Landing, Woodmansie, Whitney's, etc. The clays are white, yellow, chocolate, and black, and sometimes even lignitic. Many are buff-burning and semi-refractory, on which account they are much sought after for the manufacture of buff bricks and terra-cotta.

The Alloway clay, which extends from near Swans Mills, Gloucester County, to a point two miles south of Alloway in Salem County, is a light-brown clay, of great toughness and high plasticity. Where weathered it contains many joints often filled with iron crusts, which greatly diminish its value. The Alloway clay is a red- and dense-burning material, of rather high air- and fire-shrinkage, but excellently adapted to the manufacture of stiff-mud brick and drain-tile.

The Asbury clay is well exposed west of Asbury Park, and is usually a dark sandy clay with laminæ of sand, adapted only to common-brick manufacture.

PLEISTOCENE CLAYS

Pleistocene clays are widely scattered over the State. To the north of the terminal moraine (Fig. 140) they consist of first, basin-shaped beds occurring in the valleys; second, stony clays or till found in the glacial drift (Fig. 10); and, third, estuarine clays, occurring in great abundance in the vicinity of Hackensack. They are all impure materials adapted in most cases only to the manufacture of common brick or drain-tile.

In the region south of the terminal moraine the most important clays are those of the Cape May formation. These clays occur in a sand and gravel formation, found underlying terraces along the rivers from the coast inland to an altitude of from 40 to 60 feet. Along the Delaware River they are specially prominent, but other points are Cohansey Creek near Bridgeton, the Maurice River south of Millville, etc. The beds of clay are usually of limited extent and grade into sand.

The Cape May clays are of value chiefly for the manufacture of red brick and drain-tile, but occasionally small lenses of buff-burning clays are found.

Up to the present time no fire-clays have been found in the Cape May formation.

In the following tables will be found the analyses and physical tests of a number of representative samples of New Jersey clays:

ANALYSES OF NEW JERSEY CLAYS

	I	II	III	IV	V	VI
Sand	66.67	66.66	77.72	72.37	66.12	1.50
Combined Silica (SiO_2)						42.90
Alumina (Al_2O_3)	18.27	14.15	15.74	14.40	22.07	38.34
Ferric oxide (Fe_2O_3)	3.11	3.43	0.49	3.43	1.31	0.86
Lime (CaO)	1.18	2.15	trace	0.75	0.50	......
Magnesia (MgO)	1.09	0.38	0.81	0.49	0.25	......
Potash (K_2O)	2.92	2.32	trace	1.60	1.81	0.26
Soda (Na_2O)	1.30	1.38	trace			0.18
Titanium oxide (TiO_2)	0.85	......	......	......	......	1.20
Ignition	4.03	8.40	5.62	6.70	7.94	13.50
Moisture	......	......	......	......	......	1.10

	VII	VIII	IX	X	XI	XII
Sand	5.20	64.00	8.10	60.18	51.56	68.38
Combined Silica (SiO_2)	40.40		39.80			
Alumina (Al_2O_3)	38.40	29.08	36.34	23.23	33.13	20.11
Ferric oxide (Fe_2O_3)	1.20	1.12	1.01	3.27	0.78	1.71
Lime (CaO)	0.22	......	......	1.00	trace	......
Magnesia (MgO)	0.25	......	0.04	0.67	trace	0.73
Potash (K_2O)	0.59	2.64	0.15	2.58	trace	2.58
Soda (Na_2O)	......	......	......	0.80	trace	......
Titanium oxide (TiO_2)	*	*	*	......	1.91	1.01
Ignition	12.50	6.80	12.90	8.54	12.50	5.55
Moisture	1.30	......	1.20	......	......	......

	XIII	XIV	XV	XVI	XVII
Sand	45.76	28.81	51.80	48.40	68.96
Combined silica (SiO_2)		31.12	20.00	19.44	
Alumina (Al_2O_3)	39.05	26.95	18.92	21.83	17.87
Ferric oxide (Fe_2O_3)	trace	1.24	0.88	1.57	3.27
Lime (CaO)	0.95	......	......	0.28	0.25
Magnesia (MgO)	0.04	0.07	......	0.24	0.25
Potash (K_2O)	trace	trace	0.48	2.24	2.10
Soda (Na_2O)	trace	trace	......	......	
Titanium oxide (TiO_2)	......	1.90	......	......	......
Ignition	14.46	9.63	6.70	5.90	6.95
Moisture	......	0.57	0.50	0.80	......

* With Al_2O_3.

Localities of the Preceding

No.	Locality	Geological age	Uses	Ref.
I	Little Ferry	Pleistocene	Bricks	B 373
II	Budd Bros., Camden	Clay Marl I.	Bricks	B 396
III	H. Hylton, Palmyra	Raritan	Fire-bricks	B 392
IV	A. E. Burchem, Buckshutem	Cape May	Bricks	B 415
V	Clayville Min. & Brick Co., Clayville	Cohansey	Conduits	B 409
VI	Geo. Such, Burt Creek	South Amboy, Raritan	Ball-clay	A 198
VII	E. Roberts, Florida Grove	South Amboy, Raritan	No. 1 fire-clay	A 135
VIII	Crossman Clay Co., Sand Hills	Woodbridge	Top-white clay	A 145
IX	R. N. and H. Valentine, Sand Hills	Woodbridge	Fire-bricks	A 154
X	Sayre and Fisher, Sayreville	Woodbridge	Common brick	B 467
XI	No. 1 fire-clay, Anness and Potter, Woodbridge	Woodbridge	Fire-brick	B 441
XII	W. H. Berry, Woodbridge	Woodbridge	Sewer-pipe	A 82
XIII	W. H. Cutter, Woodbridge	Woodbridge	Ball-clay	B 443
XIV	W. B. Dixon, Woodbridge	Raritan	Fire-clay	A 79
XV	Extra sandy clay, Loughridge and Powers, Woodbridge	Woodbridge	Fire-clay	A 93
XVI	S. A. Meeker, Woodbridge	Woodbridge	Stoneware-clay	A 99
XVII	D. Haines & Son, Yorktown	Alloway	Brick and tile	B 496

A, Report on Clays of New Jersey, 1878. B, N. J. Geol. Surv., Fin. Rept., VI, 1904.

The physical tests are given on page 494.

REFERENCES ON NEW JERSEY CLAYS

1. Cook, G. H., Report on the Clay Deposits of Woodbridge, South Amboy, and other Places in New Jersey, N. J. Geol. Surv., 1877.
2. Hollick, A., Minerals from Fire-clay Beds at Green Ridge, Staten Island, Amer. Nat., XXV, p. 403, 1891.
3. Hunt, T. S., On the Origin of Clays on the Atlantic Seaboard, Amer. Inst. Min. Eng., Trans., VI, p. 188, 1879.
4. Newberry, J. S., On the Raritan Clays of New Jersey, Amer. Assoc. Adv. Sci., 1869.
5. Ries, H., Kümmel, H. B., and Knapp, G. N., The Clays and Clay Industry of New Jersey, N. J. Geol. Surv., Fin. Rept., Vol. VI, 1904.
6. Smock, J. C., Mining Clay, Amer. Inst. Min. Eng., Trans., III, p. 211.
7. Smock, J. C., Plastic Clays of New Jersey, Amer. Inst. Min. Eng., Trans., VI, p. 177.

PHYSICAL TESTS OF NEW JERSEY CLAYS

		I.	II.	III.	IV.	V.
Per cent water required		18.5	21	20	32	33
Air-shrinkage, per cent		2	2	5.3	7	3.4
Plasticity		low	fair	fair	fair	fair
Average tensile strength, lbs. per sq. in.		51	150	65	52	33
Cone 05	Fire-shrinkage, per cent	1.6	2	1.3	—	—
	Absorption, per cent	16.14	6.56	—	—	—
Cone 1	Fire-shrinkage, per cent	4.6	—	—	3	—
	Absorption, per cent	8.82	—	—	19.69	—
Cone 5	Fire-shrinkage, per cent	7	—	1.3	5	6.2
	Absorption, per cent	3.26	—	14.52	16.75	—
Cone 8	Fire-shrinkage, per cent	—	—	2	—	14.6
	Absorption, per cent	—	—	12.82	—	7.14
Cone of viscosity		—	1	27	27 +	4+
Color when burned		red	red	buff	buff	white

		VI.	VII.	VIII.	IX.	X.
Per cent water required		33	33	30.5	25.5	20
Air-shrinkage, per cent		4.4	5	4	6.5	6
Plasticity		fair	fair	good	good	good
Average tensile strength, lbs. per sq. in.		48	41	72	88	156
Cone 05	Fire-shrinkage, per cent	—	—	—	1.5	1.3
	Absorption, per cent	—	—	—	17.93	16.54
Cone 1	Fire-shrinkage, per cent	—	—	6.6	3	2.6
	Absorption, per cent	—	—	10.17	13.61	12.68
Cone 5	Fire-shrinkage, per cent	13.6	7.1	7	3.7	2.3
	Absorption, per cent	7.07	13.74	9.30	9.98	10.17
Cone 8	Fire-shrinkage, per cent	13.8*	11	8	6	—
	Absorption, per cent	6.47	9.10	—	10.70	—
Cone of viscosity		32	34 +	12	12?	8
Color when burned		buff	buff	red	red	red

		XI.	XII.	XIII.	XIV.	XV.
Per cent water required		34.9	27	23.4	27.2	22
Air-shrinkage, per cent		10	7.6	8	7	6
Plasticity		high	high	high	high	good
Average tensile strength, lbs. per sq. in.		286	229	293	291	108
Cone 05	Fire-shrinkage, per cent	3.3	1	.3	3.3	4.3
	Absorption, per cent	11.12	13.42	11.65	12.46	7.88
Cone 1	Fire-shrinkage, per cent	3.3	2.7	3.3	6	8.6
	Absorption, per cent	9.92	8.9	6.2	5.5	.10
Cone 5	Fire-shrinkage, per cent	—	—	4	7	
	Absorption, per cent	—	—	4.36	3.51	
Cone 8	Fire-shrinkage, per cent	—	5.7	5	—	
	Absorption, per cent	—	1.21	—	—	
Cone of viscosity		10	12+	—	—	3 +
Color when burned		red	red	buff	red	red

* Cone 10.

Localities of the Preceding

No.	Locality	Geological age	Uses	Ref.
I	Port Murray	Hudson River	Fireproofing	A
II	Kingsland	Triassic	Brick	B
III	H. Hylton, Palmyra	Cretaceous	Fire-brick	C
IV	C. S. Edgar, Bonhamtown	Raritan	Saggers	D
V	W. H. Cutter, Woodbridge	Woodbridge fire-clay beds	White ware	E
VI	R. H. and N. Valentine, Sand Hills, No. 1 blue clay	Woodbridge fire-clay beds	Fire-brick	F
VII	No. 1 clay, Anness and Potter, Woodbridge	Woodbridge fire-clay beds	Fire-brick	G
VIII	Sayre and Fisher, Sayreville	Woodbridge black laminated clay	Common brick	H
IX	Carman and Avery, Cliffwood	Cliffwood laminated sands and clays	Common brick	I
X	Budd Bros., Camden	Clay Marl I	Common brick	J
XI	One mile south of Collingswood	Clay Marl II	Brick and tile	K
XII	Yorktown	Alloway	Brick and tile	L
XIII	May's Landing	Cohansey	Pressed brick	M
XIV	A. E. Burchem, Buckshutem	Cape May	Common brick	N
XV	Little Ferry	Pleistocene	Common brick	O

Ref. A, N. J. Geol. Surv., Fin. Rept., VI, p. 507; B, do., p. 374; C, do., p. 392; D, do., p. 449; E, do., p. 442; F, do., p 447; G, do., p. 440; H, do., p. 467; I, do., p. 474; J, do., p. 394; K, do., p. 397; L, do., p. 495; M, do., p. 370; N, do., p. 414; O, do., p. 373.

NEW MEXICO

Adobe brick are made at many points from the calcareous valley clays, and common burned brick are also manufactured at different points. The Cretaceous shales at Las Vegas have yielded good results with the dry-press brick process. Fire-clays have been worked at Socorro and were formerly made into fire-brick.

In the San Juan district the clay industry is limited to the Animas and San Juan valleys. Surface clays are worked for brick-making at Farmington, Flora Vista, Aztec, and Fruitland, but at Shiprock the Mancos shale is employed.

At Gallup a semi-refractory clay has been mined for converter linings in the copper smelters of southern Arizona (see Analysis I below). The Mancos shale is worked for brick-making near Gallup (Analysis II), but the high carbon contents cause trouble, although they are not given in the analysis.

Analyses of New Mexico Clays

	I	II
Silica (SiO_2)	64.73	56.29
Alumina (Al_2O_3)	17.75	23.18
Ferric oxide (Fe_2O_3)	6.53	
Lime (CaO)		3.73
Magnesia (MgO)		2.91
Ignition	5.09	11.53
Moisture	4.36	
	98.46	97.64

REFERENCES ON NEW MEXICO CLAYS

1. Shaler, M. K., and Gardner, J. H., Clay Deposits of the Western Part of the Durango-Gallup Coal Fields of Colorado and New Mexico, U. S. Geol. Surv., Bull. 315, p. 296, 1906.

NEW YORK

The greater portion of New York State is underlain by sedimentary rocks of Paleozoic age, ranging from the Cambrian to the Carboniferous inclusive. These consist in very large part of shales, but sandstones and limestones are at times prominent. The Cretaceous and Tertiary formations, so abundant in States farther south, are found in New York only on Staten Island, Long Island, and Fisher's Island.

Overlying all of the above are Pleistocene deposits. Residual clays are rare. The clay-deposits of the State may, therefore, be grouped as follows: Residual clays, Paleozoic shales, Cretaceous, Tertiary clays, and Pleistocene clays.

Residual Clays

These are of but little importance in New York State, and may be passed over with the statement that some deposits of kaolin have been found east or southeast of Sharon, but so far as known none have ever proven of economic value.

Paleozoic Shales

Those occurring in New York State and including beds of value to the clay-worker belong to the Medina, Salina, Hamilton, Portage, and Chemung. The Hudson, Clinton, and Niagara formations are of little or no value for the manufacture of clay-products. All of these shale formations, with the exception of the Hudson, form bands of variable width extending across the State in an east-west direction, and their distribution can best be seen by reference to the geologic map of New York, from which it will appear that the oldest formations outcrop towards the north, in belts running parallel to Lake Ontario. Their characters are briefly as follows:

Hudson River shale.—This formation, although widely distributed in the eastern part of the State, is of no economic value for the manufacture of clay-products, since it is deficient in plasticity and is very siliceous.

Niagara shale.—This also, on account of its calcareous and siliceous character, is of little or no value.

Medina shale.—Along the Niagara River at Lewiston, and also along the Genesee River, there are outcrops of this rock. It is not utilized in New York State, but has given good results for dry-pressed brick in Ontario.

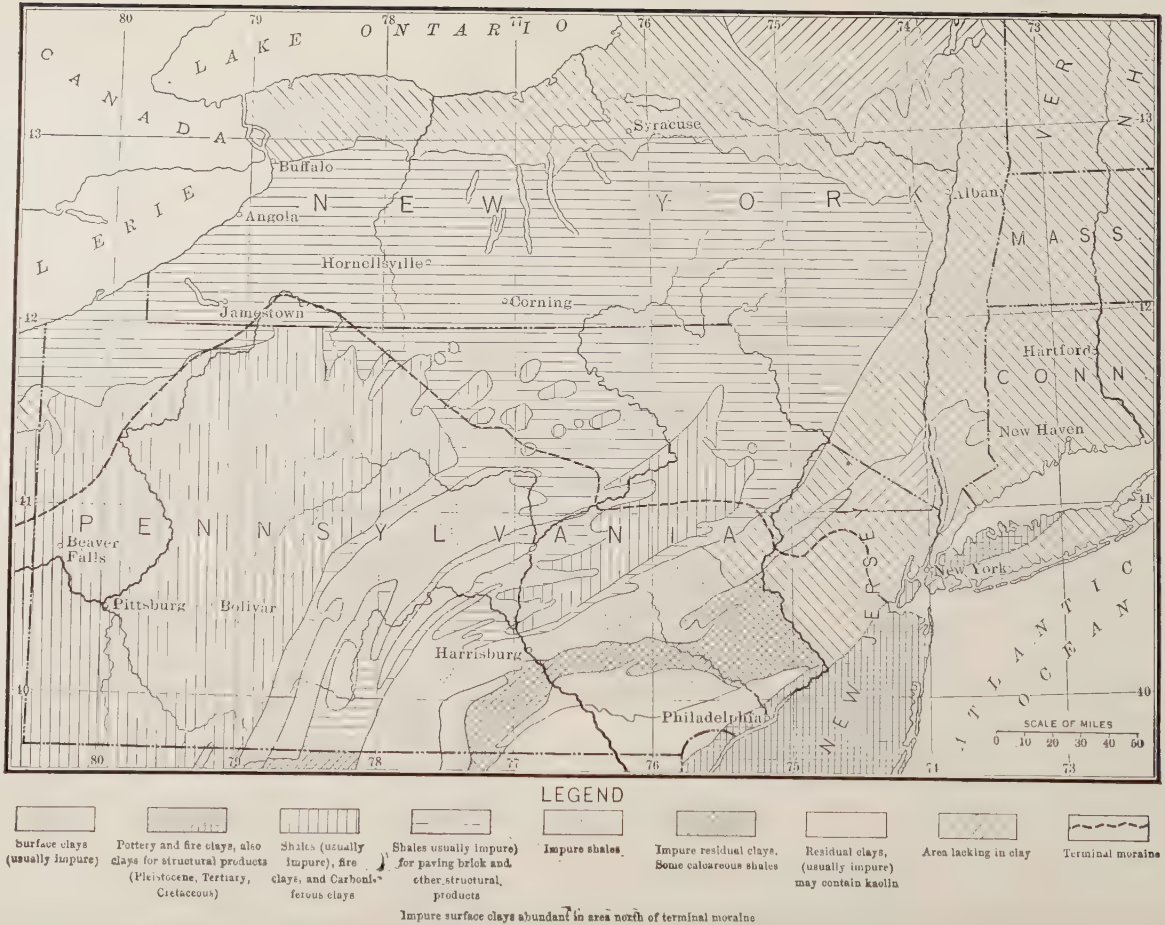
Clinton shales.—These are about 30 feet thick in places, notably in eastern Wayne County, and 24 feet thick at Rochester and Wolcott Furnace. They have not been used and are probably often calcareous.

Salina shales.—This series forms a belt extending from Syracuse westward. The shale is soft, weathers easily, and possesses good plasticity, but may be quite calcareous, and not infrequently carries lumps of selenite. It is red-burning, and has been used for common brick, drain-tile, or conduits.

Hamilton shale.—Though extending from the Hudson River to Lake Erie, this formation shows considerable lithologic variation ranging from a sandstone to a clay-shale. The latter phase is more common in the western part of the State. It was worked for paving-brick at Cairo, Greene County, and beds of good quality are known at Windom, Erie County.

Portage shale.—This overlies the Hamilton stratigraphically, and hence outcrops to the south of the Hamilton belt. It consists of shales and sandstones, the former being well exposed along Cashaqua Creek, also along Seneca Lake and at Penn Yan, but becomes very gritty east of this point. The shale is worked at Angola for draintile and hollow brick, at Jewettville for pressed brick, at Binghamton for paving-bricks and face-brick, and at Jamestown for pavers.

Chemung shale.—This somewhat extensive shale formation, the most southern in New York State, has been utilized at several points for making clay-products. At Corning face-brick are made.


CANADA
LAKE ONTARIO
LAKE ERIE
NEW YORK
PENNSYLVANIA
NEW JERSEY
MASS.
CONN.
VERMONT
N. H.
ATLANTIC OCEAN
Syracuse
Buffalo
Angola
Hornellsville
Corning
Jamestown
Albany
Hartford
New Haven
New York
Beaver Falls
Pittsburg
Bolivar
Harrisburg
Philadelphia
80
79
78
77
76
75
74
73
71
43
42
41
40
SCALE OF MILES
0 10 20 30 40 50
LEGEND
Surface clays (usually impure)
Pottery and fire clays, also clays for structural products (Pleistocene, Tertiary, Cretaceous)
Shales (usually impure), fire clays, and Carboniferous clays
Shales usually impure) for paving brick and other structural products
Impure shales
Impure residual clays, Some calcareous shales
Residual clays, (usually impure) may contain kaolin
Area lacking in clay
Terminal moraine
Impure surface clays abundant in area north of terminal moraine

CRETACEOUS AND TERTIARY CLAYS

These include the Cretaceous clays of the Coastal Plain region of Long Island, Staten Island, and Fisher's Island, as well as some others of possible Tertiary age, but the deposits are of exceedingly variable character, ranging from ferruginous ones to others of good refractoriness. They, moreover, partake of the character of other Coastal Plain clays in being often of highly siliceous character as well as pockety or lens shaped in form. The more important points at which these clays are exposed are at Kreischerville, Staten Island; Little Neck near Northport, West Neck, Oyster Bay, Wyandance, and Farmingdale, Long Island. All of these, except the first two, are adapted only to the manufacture of common brick. The deposits of Glencove and Northport have been worked for a number of years, those of the latter locality having been used for fire-brick, stove-linings, and stoneware.

PLEISTOCENE CLAYS

These can be divided into four groups, namely, (1) morainal clays; (2) lacustrine clays; (3) pond deposits; (4) estuarine deposits.

The morainal clays are usually too stony to be of any value, although at Newfield, Tompkins County, one lens in the moraine was worked for fifteen years.

The lacustrine clays were laid down during post-Glacial time, when the waters of Lakes Erie and Ontario were dammed up to the north by the retreating continental glacier, and spread over the land in the western and northwestern part of the State, much clay being deposited during this time. These clays underlie the flats around Buffalo, Lancaster, Tonawanda, and other places in western New York, and are used for making brick and drain-tile. They often contain lime pebbles.

The pond deposits are widely distributed throughout the State, being found in many of the flat-bottomed valleys. They are prevailingly impure, often contain sandy streaks, and are rarely deep. Most of them burn red and are worked for common brick or tile, but hollow brick are also manufactured.

Laminated clays are wide-spread in the Hudson River and Champlain Valleys, and were deposited during post-Glacial times. They form an extensive and often thick deposit, which underlies the terraces bordering these valleys (Fig. 145). The section usually involves an upper sand-bed, a yellow weathered clay, and a blue clay. The clays are

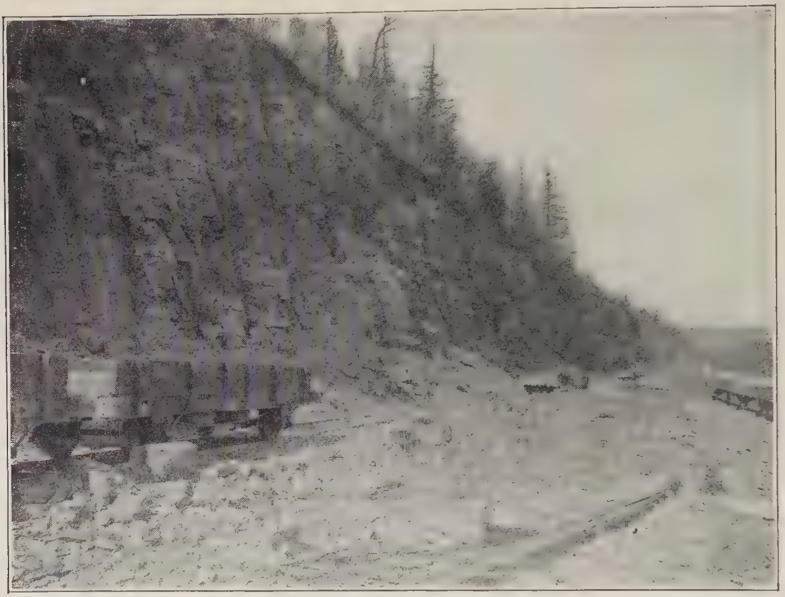


FIG. 144.—Bank of Chemung shale used for brick, Corning, N. Y. (After H. Ries, N. Y. State Mus., Bull. 35, p. 838, 1900.)

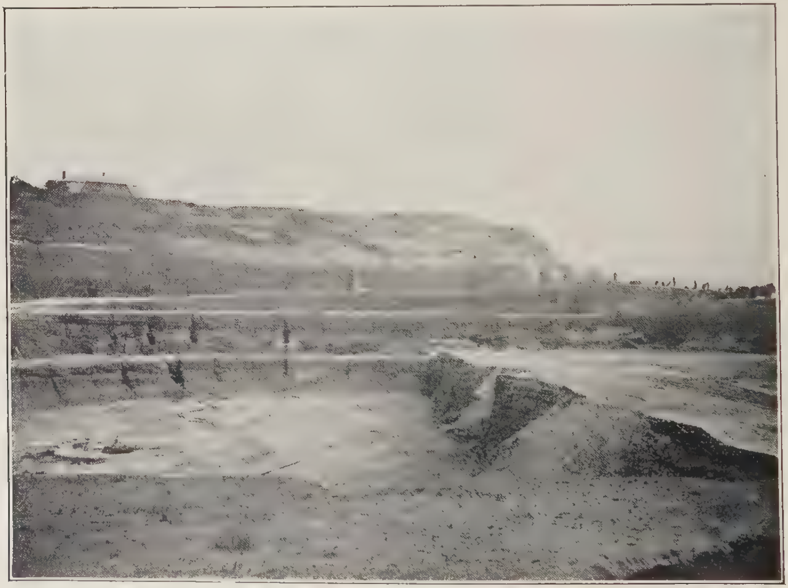


FIG. 145.—Bank of Pleistocene clay overlain by sand, Roseton, N. Y. (After H. Ries, N. Y. State Mus., Bull. 35, p. 698, 1900.)

laminated materials, plastic, red-burning, and easily fusible. Those in the Hudson Valley especially are extensively dug for the manufacture of common brick, but are probably useless for much else, although certain beds near Albany make an admirable slip-clay which is shipped to all parts of the United States.

In the following tables there are given a number of selected analyses and physical tests of New York clays:

ANALYSES OF NEW YORK CLAYS *

	I	II	III	IV	V
Silica (SiO_2)	59.50	52.30	65.15	53.20	68.34
Alumina (Al_2O_3)	20.60	18.35	15.29	23.25	19.89
Ferric oxide (Fe_2O_3)	8.00	6.55	6.16	10.90	0.90
Lime (CaO)	0.80	3.36	3.50	1.0	0.35
Magnesia (MgO)	0.35	4.49	1.57	0.62	trace
Potash (K_2O)	3.60	4.65	5.71	2.69	3.55
Soda (Na_2O)		1.35			0.84
Combined water (H_2O)	5.50	+organic 5.30	....	6.39	6.03
Miscellaneous	....	CO_2 3.04	....	MnO_2 0.52 TiO_2 0.91 SO_3 0.41	

	VI	VII	VIII	XI	X
Silica (SiO_2)	47.40	55.00	51.61	57.36	51.30
Alumina (Al_2O_3)	39.01	34.54	19.20	16.20	12.21
Ferric oxide (Fe_2O_3)	0.15		8.19	4.55	3.32
Lime (CaO)	trace	5.33	7.60	5.34	11.63
Magnesia (MgO)	trace	3.43	1.5	3.90	4.73
Potash (K_2O)	trace	0.48	5.32	6.98	4.33
Soda (Na_2O)	trace				
Combined water (H_2O)	14.10	1.22	$+CO_2$ 7.25		
Moisture	....				
Miscellaneous	....	....	....	....	organic 1.50

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* From N. Y. State Mus., Bull. 35.

Physical Tests of the Above

	I	III	IV	VI
Per cent H_2O to form plastic mass	16	21.4	20	38
Plasticity	lean	fair	moderate	fair
Average tensile strength, pounds per square inch	15	92	61	11–14
Air-shrinkage	3	4	4	10
Fire-shrinkage	6	10	9	8.7
Incipient fusion	cone .04	06	06	....
Vitrification	1	01	01	35+
Viscosity	4	4	3	35+

Localities of the Preceding

No.	Locality	Geological age	Uses *
I	Lewiston	Medina	Not worked
II	Warners	Salina	Paving, common, and hollow brick
III	Angola	Portage	Flue-linings
IV	Alfred Center	Chemung	Roofing tile
V	Near Northport	Cretaceous	Stoneware
VI	Kreischerville	Cretaceous	Fire-brick
VII	Roseton	Pleistocene	Common brick
VIII	Croton Point	Pleistocene	Common brick
IX	Buffalo	Pleistocene	Common brick
X	Newfield	Pleistocene (drift)	Common and paving brick

* Some of these are no longer worked.

REFERENCES ON NEW YORK CLAYS

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2. Jones, C. C., A Geologic and Economic Survey of the Clay-deposits of the Lower Hudson River Valley, Amer. Inst. Min. Eng., Trans., XXIX, p. 40, 1900.
3. Martin, D. S., A Note on the Colored Clays Recently Exposed at Morrisania, N. Y. Acad. Sci., Trans., IX, p. 46.
4. Merrill, F. J. H., Origin of the White and Variegated Clays of the North Shore of Long Island, N. Y. Acad. Sci., Annals, XII, p. 113, 1900.
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6. Prosser, C. S., Distribution of Hamilton and Chemung Series of Central New York, N. Y. State Geologist, 15th Ann. Rept., p. 87, 1899.
7. Ries, H., Clays of New York, Their Properties and Uses, N. Y. State Museum, Bull. 35, 1900.

8. Ries, H., Physical Tests of Devonian Shales of New York State, 15th Ann. Rept., N. Y. State Geologist, Vol. I, p. 673, 1897.
9. Ries, H., On the Occurrence of Cretaceous Clays at Northport, Long Island, School of Mines Quart., XV, p. 354, 1894.

NORTH CAROLINA[1]

The clay deposits found in North Carolina are of two types, namely, residual clays and sedimentary clays or shales.

Residual Clays

These may occur in any portion of the State west of the Coastal Plain region. The eastern border of this area passes through Halifax, Franklin, Wait, Chatham, Moore, and Anson. Most of the residual clays are ferruginous and often gritty.

A noteworthy exception to the above occurrences are the deposits of white residual clay—kaolin—which are derived usually from the weathering of pegmatite, and are found in both the Mountain and Piedmont provinces, although only the former group is commercially important.

The bodies of pegmatite which consist of quartz, feldspar, and mica (usually muscovite) with occasionally garnet and tourmaline have been weathered to kaolin to a depth of 60 to 100 feet. The vein-like masses may vary in width from a few inches to several hundred feet, and may be several hundred feet long. They also branch or curve and pinch or swell. The most active kaolin mines are in Haywood, Jackson, Mitchell and Yancey counties. All of the kaolin needs washing before shipment to market, and the product is extensively used in the whiteware industry.

The following tests of two samples were made by the Bureau of Mines Station at Columbus, Ohio:

	I	II
	Per cent	Per cent
Water plasticity, terms of dry clay	43.18	44.48
Volume air shrinkage, terms of dry clay	14.11	20.20
Linear air shrinkage, calculated	5.0	7.3
Fineness test:		
Residue 20-mesh-sieve	21.18	0.0
Residue 65-mesh sieve	29.87	0.0
Residue 100-mesh sieve	2.28	0.0
Residue 200-mesh sieve	.....	2.92
Amount passing 200-mesh sieve	46.67	97.08

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[1] Prof. J. L. Stuckey has supplied much recent information regarding this State.

Firing Tests

	Porosity, per cent	Volume fire shrinkage, per cent	Porosity, per cent	Volume fire shrinkage, per cent
1190° C.	45.90	10.7	39.6	18.1
1250° C.	47.20	8.1	39.7	18.4
1310° C.	44.87	14.0	37.97	20.3
1370° C.	40.80	22.3	35.5	24.98
1410° C.	29.10	24.5	28.5	28.0

I. Crude kaolin, Sprucepine, Mine No. 1, Mitchell County, N. Ca.
II. Washed kaolin, Sparks plant, Sprucepine, Mitchell County, N. Ca.

PRE-CAMBRIAN SHALES

Shales of pre-Cambrian age are found in what is known as the " Slate belt " which crosses the central part of the State from southwest to northeast, and their development has taken place in the last few years. The shales can be easily made into good common brick and face brick if thoroughly pugged. The slightly weathered material gives no trouble in firing, but the harder (less weathered) shale has a shorter firing range, due to more fluxes, and often does not stand over 1850° F. The shales burn red. It is suggested that they can also probably be used for making drain-tile, roofing-tile, and hollow blocks (Ref. 4).

CAMBRIAN

These are found at a number of localities in the western part of the State, and especially in Madison County. They fire red and could probably be used for heavy structural clay products (Ref. 4).

TRIASSIC

In the Dan River coal field the red-burning Triassic shales are worked for making various structural clay products and sewer-pipe. They are manufactured at Pomona, from shales obtained at Madison, Rockingham County, and now also at Pine Hall.

In the Deep River coal field of Moore, Chatham, and Lee counties, there is another shale area, which although not as extensively developed is considered very promising. It is now being worked at several points for brick, and hollow blocks, and some of the shale is shipped to Pomona

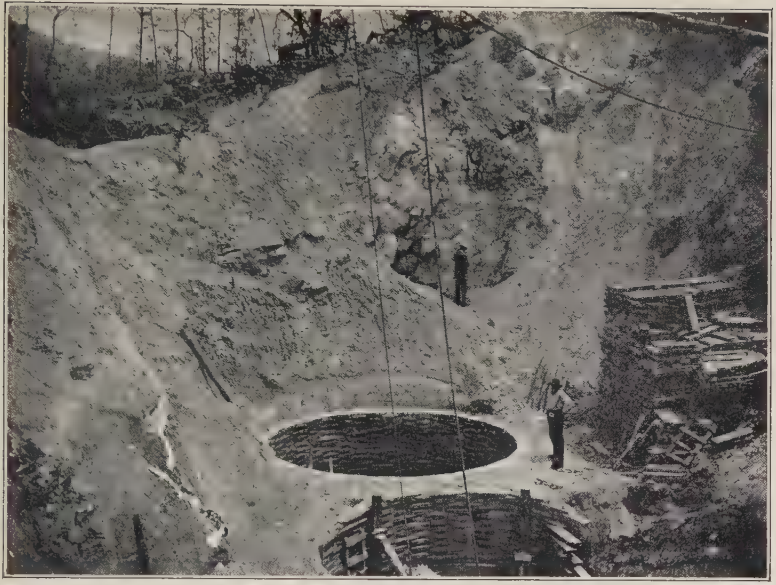

FIG. 146.—Kaolin-mine near Webster, N. C., showing kaolin mining by circular pits. (After Ries, N. C. Geol. Surv., Bull. 13, p. 56, 1897.)

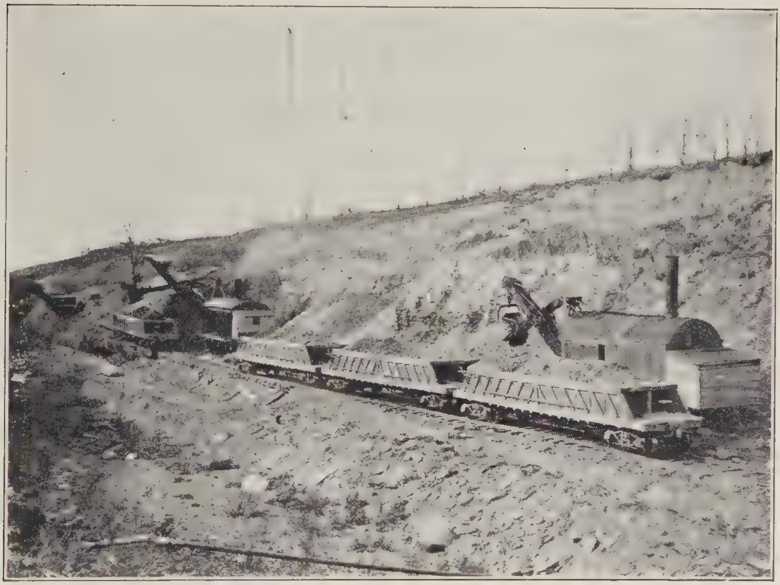

FIG. 147.—Bank of Carboniferous shale near Akron, O. (Photo loaned by Robinson Clay-product Co.)

for sewer-pipe. The shale fires red and gives a hard body around 1800° F. Art pottery is made near Sanford.

MESOZOIC TO PLEISTOCENE

Beds of plastic clay are found widely distributed throughout both the Coastal Plain area, and the broader upland valleys of the State. In the former there are many extensive beds of laminated clay which are often well exposed in the river-banks traversing the region. Most of the clay deposits found in the Coastal Plain area are rather lenticular in their form and pass horizontally into beds of sand. Among those which have been developed may be mentioned the deposits at Fayetteville, Goldsboro, Weldon, Greensboro, etc. They are nearly all red-burning and have been used for the manufacture of brick and drain-tile.

In many valleys of the uplands the rivers are bordered by terraces underlain by clays of Pleistocene age, such clays being abundant along the Catawba River near Morgantown and Mount Holly, on the Clark River, at Lincolnton, along the French Broad at Asheville, and along the Yadkin at Wilkesboro. The depth of these terrace clays commonly ranges from 5 to 10 feet, and there is usually a slight covering of sandy loam. The majority are adapted only to the manufacture of common brick, but occasionally some of them have been utilized for common stoneware.

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2. Pratt, J. H., The Mining Industry of North Carolina, N. Ca. Geol. Surv., separate bulletins on Economic Geology issued in 1901 and subsequent years.
3. Ries, H., Clay-deposits and Clay Industry of North Carolina, N. Ca. Geol. Surv., Bull. 13, 1897.
4. Stuckey, J. L., Shales of North Carolina, Jour. Amer. Ceram. Soc., Vol. VIII, p. 843, 1925.
5. Watts, A. S., Mining and Treatment of Feldspar and Kaolin in the Southern Appalachian Region, U. S. Bur. Mines, Bull. 53.

Analyses of North Carolina Clays

ULTIMATE ANALYSES

	I.	II.	III.	IV.	V.
Silica (SiO_2)	53.07	45.70	56.81	50.17	64.93
Alumina (Al_2O_3)	29.54	40.61	20.62	28.77	17.08
Ferric oxide (Fe_2O_3)	1.27	1.39	6.13	2.88	5.57
Lime (CaO)	0.15	0.45	0.65	0.05	0.43
Magnesia (MgO)	0.14	0.09	0.58	0.22	0.59
Potash (K_2O)	1.28	2.82	4.47	1.04	3.85
Soda (Na_2O)	0.87				
Combined water, ignition	9.93	8.98	8.60	14.03	6.58
Moisture	1.29	0.35	1.64	2.08	2.48
Miscellaneous	FeO 1.00				

	VI.	VII.	VIII.	IX.	X.
Silica (SiO_2)	58.17	59.27	70.45	69.58	53.75
Alumina (Al_2O_3)	20.10	22.31	17.34	14.03	24.91
Ferric oxide (Fe_2O_3)	7.43	6.69	3.16	6.41	7.99
Lime (CaO)	0.60	0.25	0.25	0.40	0.70
Magnesia (MgO)	0.77	0.13	0.22	0.27	1.12
Potash (K_2O)	2.60	0.90	0.70	1.65	2.94
Soda (Na_2O)					
Combined water, ignition	7.34	9.00	6.63	5.73	7.60
Moisture	3.23	1.90	0.93	1.68	1.03
Miscellaneous	....	....	FeO 0.33		

RATIONAL ANALYSES

	I.	II.	III.	IV.	V.
Clay substance	61.99	96.81	58.85	73.19	53.13
Free sand	36.55	25.40	40.65	26.05	45.90

	VI.	VII.	VIII.	IX.	X.
Clay substance	48.09	67.20	48.26	45.47	34.04
Free sand	52.15	33.25	51.50	51.28	46.00

Nos. I–X from N. C. Geol. Surv., Bull. 13, 1897.

PHYSICAL TESTS OF NORTH CAROLINA CLAYS

	I.	II.	IV.	V.
Per cent water for working	28	42	30	28
Plasticity	good	lean	very good	good
Air-shrinkage, per cent	8	6	12	8.5
Fire-shrinkage, per cent	5	4	7	5
Average tensile strength, lbs. per sq. in.	39	20	148	144
Rate of slaking	slow	slow	slow	fast
Texture	fine	very fine	fine	medium
Incipient fusion, degrees F.	2100	2300	1950	1900
Vitrification, degrees F.	2300	2500	2100	2050
Viscosity, degrees F.	2500	2700+	2250	2200
Color when burned	whitish	white	gray brown	red
Specific gravity	2.24	2.43	2.35	2.55

	VI.	VII.	VIII.	IX.	X.
Per cent water for working	28.5	28	26	36	25
Plasticity	fair	lean	lean	slight	lean
Air-shrinkage, per cent	9.8	10	10	9.6	5
Fire-shrinkage, per cent	7	6	2	4.5	10
Average tensile strength, lbs. per sq. in.	84	66	47	60	74
Rate of slaking	slow	fast	slow	fast	fast
Texture	fine	coarse	coarse	fine	fine
Incipient fusion, degrees F.	1850	2100	2150	1950	1900
Vitrification, degrees F.	2050	2400	2350	2100	2100
Viscosity, degrees F.	2250	2500	2550	2250	2300
Color when burned	red	red	buff	red	deep red
Specific gravity	2.45	2.46	2.55	2.59	2.63

LOCALITIES OF THE PRECEDING.

No.	Locality.	Geological Age.	Uses.
I.	Grover	Residual	White pressed brick
II.	Webster	"	White ware
III.	Greensboro	"	Brick
IV.	N.W. of Blackburn		Stoneware
V.	Fayetteville (average)		Bricks
VI.	Fayetteville		Not worked
VII.	Greensboro	Pleistocene	Brick
VIII.	Pomona		Brick
IX.	Morgantown	Columbia	Not worked
X.	Wilkesboro	"	" "

Nos. I–X from N. C. Geol. Surv., Bull. 13, 1897.

CHAPTER IX

NORTH DAKOTA TO WYOMING

NORTH DAKOTA

The North Dakota clays (Ref. 2) are found in the Cretaceous, Tertiary and Pleistocene formations (Fig. 148).

Cretaceous

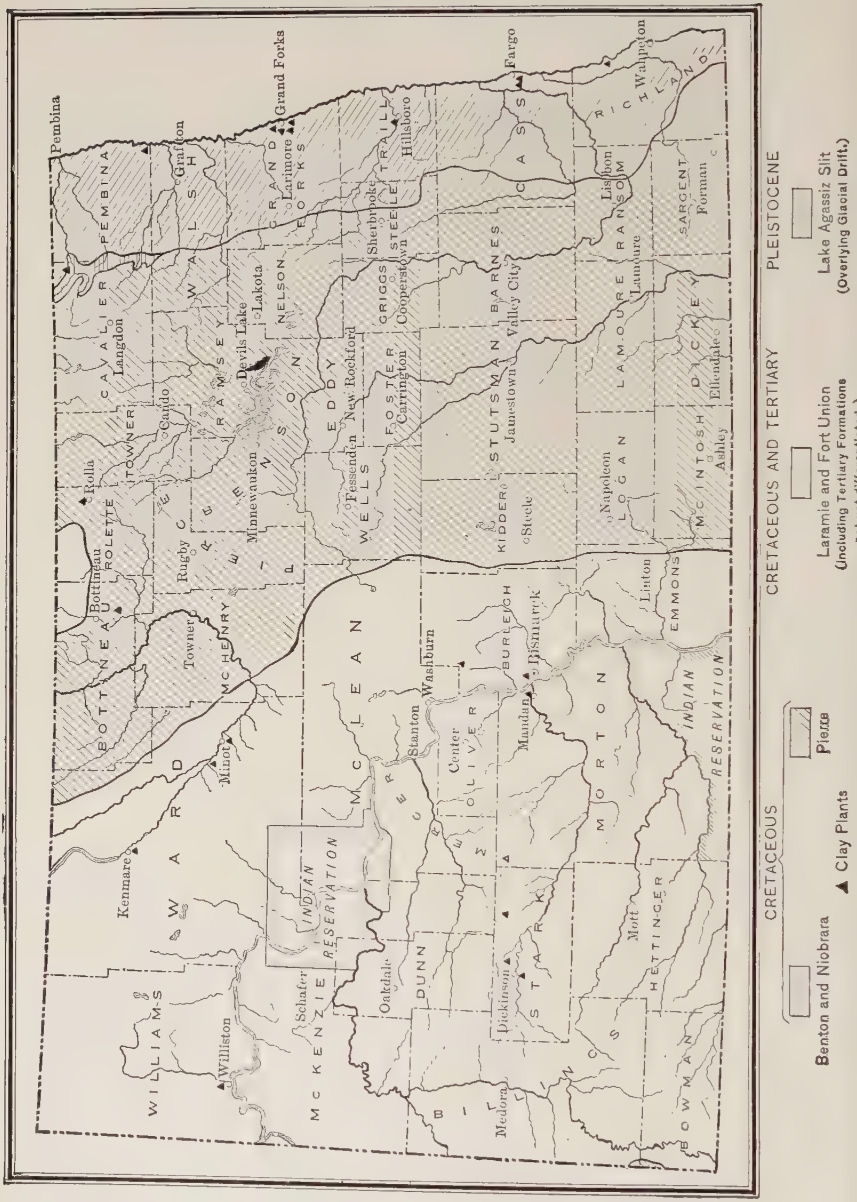
Most of the divisions of this system of rocks carry extensive deposits of clay, whose character is briefly as follows:

The Benton, Niobrara and Pierre clay-bearing formations extend across the east central part of the State in a broad belt several hundred miles wide (Fig. 148).

Benton.—The Benton is best developed in the Pembina Mountains, where it shows about 150 feet of soft shales which are easily mined. Ferruginous concretions and gypsum are not uncommon, in fact the latter is present in such quantity near top of the formation as to render the shales nearly worthless. The Benton shales are plastic, red-burning, and yield a hard body at low temperatures, in fact their use for vitrified brick is regarded as possible.

Niobrara.—This formation overlies the Benton, but is not sharply separated from it. It is usually calcareous, and may carry from 20–75 per cent of lime carbonate.

Fierre.—The Pierre shales are separated from the underlying Niobrara by a peculiar horizon of banded black, white and red shales. The maximum thickness of 300 feet is developed in the Pembina Mountains, but it is exposed at other points. The shales which are quite uniform in character, and of a dark gray or black color, contain many small iron concretions, and are usually low in lime except near the base. They are very plastic, with high air and fire-shrinkage, and red-burning. Much trouble is caused in burning by gypsum and pyrite. The lowest beds are the worst, but about 200 feet from the bottom of the formaticn the clay is lighter colored, has less impurities and is semi-refractory.


Pembina
Grand Forks
Fargo
Wahpeton
PEMBINA
CAVALIER
Langdon
Grafton
WALSH
GRAND FORKS
Larimore
TRAILL
Hillsboro
Lakota
NELSON
Devils Lake
RAMSEY
Cando
TOWNER
Rolla
ROLETTE
Bottineau
BOTTINEAU
Rugby
PIERCE
BENSON
Minnewaukon
Towner
MCHENRY
EDDY
New Rockford
Sherbrooke
STEELE
GRIGGS
Cooperstown
CASS
BARNES
Valley City
FOSTER
Carrington
Fessenden
WELLS
STUTSMAN
Jamestown
KIDDER
Steele
Lisbon
RANSOM
RICHLAND
SARGENT
Forman
LAMOURE
Lamoure
DICKEY
Ellendale
LOGAN
Napoleon
MCINTOSH
Ashley
EMMONS
Linton
BURLEIGH
Bismarck
Mandan
MORTON
INDIAN RESERVATION
MCLEAN
Washburn
Stanton
Center
OLIVER
MERCER
WARD
Minot
Kenmare
INDIAN RESERVATION
MCKENZIE
Schafer
Oakdale
DUNN
STARK
Dickinson
HETTINGER
Mott
WILLIAMS
Williston
BILLINGS
Medora
SLOPE
BOWMAN
CRETACEOUS
Benton and Niobrara
Pierre
CRETACEOUS AND TERTIARY
Laramie and Fort Union (Including Tertiary Formations not yet differentiated.)
PLEISTOCENE
Lake Agassiz Silt (Overlying Glacial Drift.)
▲ Clay Plants

LARAMIE AND TERTIARY

Nearly the entire western half of the State is underlain by strata of Laramie and Tertiary age, the exact boundary between the two being doubtful. Lithologically, the so-called Laramie consists of (1) a basal member of clays and sands, many of them calcareous and lignitic; (2) a series of beds not exceeding 150 feet in thickness, carrying high grade, light-burning and sometimes refractory clays; (3) 300 or 400 feet of sand, cemented in part by calcareous cement. The clays of the first two divisions are of value for little else than common brick. Those of the third are an important clay resource of the State, being regarded by Mr. Clapp as of value for making pressed brick, fire-brick and pottery. They occupy an area approximately 50 miles east-west by 90 miles north-south, the eastern limit being about on the meridian passing through Hebron. These clays lie on both sides of the Northern Pacific railroad and have been developed around Dickinson, Gladstone and Hebron.

PLEISTOCENE

Pleistocene clays of blue or yellow color, and often of gravelly or stony character, are found over a large portion of the State. They are frequently calcareous, and around Grand Forks are worked for cream-colored brick. Red-burning brick clays occur along the Missouri River, near Bismarck, and are much used. Grayson, Walhalla and Fargo are also promising localities.

The following analyses and tests, from the Fourth Biennial Report of the North Dakota Geological Survey, have been selected by C. H. Clapp as representative.

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1. Babcock, E. J., First Biennial Report, N. Dak. Geol. Surv., p. 29, 1901.
2. Babcock, E. J., Clapp, C. H., Leonard, A. G., The Clays of North Dakota, N. Dak. Geol. Surv., 4th Biennial Rept., 1906.
3. Clapp, C. H., The Clays of North Dakota, Econ. Geol., II, p. 551, 1907.

REFERENCES TO TABLE OF ANALYSES OF NORTH DAKOTA CLAYS

I. Dickinson Brick Co., Dickinson.
II. Typical of white sandy Tertiary clay.
III. Black Butte.
IV. Buttes between Gladstone and Dickinson, north of railroad.
V. Hebron Brick Company's clay bank.
VI. Buttes, 1½ miles north of Taylor.
VII. Buttes, 2 miles north of Gladstone.
VIII. Breaks of Little Missouri River at Mannings' ranch.
I–VIII, Tertiary clays.
IX. Benton clay. Mayo Brick Co.
X. Pierre clay (representative), Jamestown.
XI. Laramie clay. Mott.
XII. Laramie clay. Coal mine at Richardton.
XIII. Pleistocene clay. Grand Forks.
I–XIII from Vol. 4, N. Dak. Geol. Surv.

Physical Tests of North Dakota Clays

	Number.	I.	II.	III.	IV.
	Per cent water required	25.2	22.6	18.9	22.1
	Per cent air-shrinkage	4.7	2.	3.8	5.
	Tensile strength, lbs. per sq. in	138	90	110	141
	Plasticity	very good	fair	good	very good
Cone 05	Fire-shrinkage, per cent	1	−.3	....	0.
	Color	light pink	pink white	....	orange
	Absorption, per cent	....	19.8	....	....
Cone 03	Fire-shrinkage, per cent	....	....	.3	....
	Color	....	....	white	....
	Absorption, per cent	....	....	....	....
Cone 1	Fire-shrinkage, per cent	6.	.9	.5	1.7
	Color	buff white	cream white	yellow	yellow
	Absorption, per cent	....	....	14.	....
Cone 5	Fire-shrinkage, per cent	6.6	2.	2.8	5.3
	Color	gray white	white	buff	buff
	Absorption, per cent	2.4	14.1	12.4	4.7
Cone 10	Fire-shrinkage, per cent	9	2.5	2.9	5.
	Color	white	white	buff brown	yellow gray
	Absorption, per cent	.5	13.1	9.3	3.4
Fusibility cone	Incipient	3	....	17	7
	Vitrification	12	....	....	16
	Viscosity	25	unaffected 25	....	25+

	Number.	V.	VI.	VII.	VIII.
	Per cent water required	20.6	27.9	26.7	25.9
	Per cent air-shrinkage	3.8	5.2	5.	4.8
	Tensile strength, lbs. per sq. in	122	91	78	90
	Plasticity	good	good	good	good
Cone 05	Fire-shrinkage, per cent	0	1.8	.8	1.7
	Color	cream	cream	pink white	red
	Absorption, per cent	15.9	....	....	13.0
Cone 03	Fire-shrinkage, per cent	.8	2.4	.9	1.5
	Color	buff	cream	pink white	light red
	Absorption, per cent	....	17.2	....	....
Cone 1	Fire-shrinkage, per cent	1.*	2.4*	3.3*	2.5*
	Color	light buff	cream white	cream white	salmon
	Absorption, per cent	....	....	14.1	....
Cone 5	Fire-shrinkage, per cent	2.9	8.2	5.9	4.7
	Color	light buff	cream	cream white	light brown
	Absorption, per cent	10.6	4.7	6.1	6.1
Cone 10	Fire-shrinkage, per cent	5.8	8.3	8.9	5.9
	Color	gray white	gray white	gray	brown black
	Absorption, per cent	1.8	1.1	1.8	3.8
Fus. cone	Incipient	8	4	3	11
	Vitrification	15	15	16	13
	Viscosity	25+	25+	25+	18

* Cone 01.

Physical Tests of North Dakota Clays—*Continued*

	Number.	IX.	X.	XI.	XII.	XIII.
	Per cent water required	46.3	45.6	26.5	29.0	25.1
	Per cent air-shrinkage	5.7	5.3	5.1	4.0	2.7
	Tensile strength, lbs. per sq. in.	108	89	110	133	127
	Plasticity	fair	good	good	good	fair
Cone 010	Fire-shrinkage, per cent	2.3	1.	.9	.9	−.5
	Color	orange red	orange	light red	light red	orange
	Absorption, per cent	....	....	18.8	23.1	31.4
Cone 05	Fire-shrinkage, per cent	4.3	4.	.9	5.4	−1.
	Color	orange red	orange	light red	light red	pink
	Absorption, per cent	21.8	26.2	18.9	10.9	33.1
Cone 03	Fire-shrinkage, per cent	5.5	4.5	6.7	7.3	−.6
	Color	red	orange red	red	red	cream
	Absorption, per cent	18.9	24.2	5.4	11.1	22.5
Cone 01	Fire-shrinkage, per cent	7.3	5.8	....	9.8	2.0
	Color	red brown	red	....	red brown	cream to green
	Absorption, per cent	15.8	21.6	....	1.5	17.9
Cone 5	Fire-shrinkage, per cent	9.3	6.8			
	Color	dark brown	brown			
	Absorption, per cent	8.5	19.8			
Fus. cone	Incipient	5	7	02	06	1
	Vitrification	8	15	1	1	3
	Viscosity	14	220	3	5	4

Analyses of North Dakota Clays.

	I.	II.	III.	IV.	V.	VI.
Silica (SiO_2)	64.84	73.20	60.98	75.27	73.90	65.46
Alumina (Al_2O_3)	24.31	18.56	26.24	17.29	16.49	20.97
Ferric oxide (Fe_2O_3)	1.60	.50	1.34	.83	1.25	1.83
Lime (CaO)	.11	.29	.34	.46	.29	.23
Magnesia (MgO)	.24	.52	.94	.18	.46	1.14
Soda (Na_2O)	.32	.38	1.22	trace	.22	.72
Potash (K_2O)	trace	.36	1.26	.32	1.20	1.38
Loss on ignition	8.58	5.93	7.85	5.75	5.52	6.79
Total	100.00	99.74	100.17	100.10	99.33	98.52

	VII.	VIII.	IX.	XI.	XII.	XIII.
Silica (SiO_2)	65.64	53.32	69.90	57.94	61.67	51.27
Alumina (Al_2O_3)	22.74	23.76	10.66	17.46	17.41	9.33
Ferric oxide (Fe_2O_3)	1.66	9.30	2.32	4.58	3.65	3.52
Lime (CaO)	.29	.25	1.04	4.14	2.32	11.15
Magnesia (MgO)	.61	1.26	2.10	3.84	3.71	2.31
Soda (Na_2O)	1.76	.10	undet.	....	....	2.08
Potash (K_2O)	1.46	2.10	undet.	....	....	.50
Loss on ignition	6.15	8.50	6.09	7.67	6.07	
Total	100.31	98.59	92.11	95.65	94.83	

For references to tables, see p. 441.

OHIO[1]

The geologic scale of Ohio includes strata ranging from the Ordovician to the Permian, while overlying these are beds of Quaternary age.

ORDOVICIAN AND SILURIAN

The rocks of these two ages underlie a large area in the western half of the State, those of the former age being found chiefly in the southwestern part. They include several shale formations, among them the Eden, Lorraine, Richmond, Saluda, and Osgood; but most of these are highly calcareous and of little value for the manufacture of clay-products. The Saluda has been used for drain-tile.[2] The Eden shale is used at Cincinnati for making dry-press building and face brick.

DEVONIAN

The Devonian rocks underlie a large area in the northwestern corner of the State, and also extend across the west-central part from Lake Erie to the Ohio River.

The shale formations are the Oletangy and the Ohio. The former is 20 to 35 feet thick in central Ohio with numerous outcrops and shows even greater thickness in the northern part of the State. It is worked at Delaware for making drain-tile, fireproofing and hollow block.

The Ohio shale is divisible, in the northern part of the State at least, into three parts, known as the Huron, Chagrin, and Cleveland shales. Professor C. S. Prosser states that the Chagrin shale is gray to greenish, and extends from the Black River as surface outcrops along the shore of Lake Erie in a belt several miles broad to Pennsylvania, and is regarded as promising for the manufacture of clay-products. It is used for building brick, building blocks, and fireproofing. The Ohio shale was formerly mixed with glacial clay and used for sewer-pipe at Columbus.

MISSISSIPPIAN

The Bedford shale, which is an important shale formation extending clear across the State, is in part at least frequently of red color; but its greenish phases resemble the Chagrin shales of similar color. It is extensively worked in the Cleveland district for making building brick,

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[1] Profs. E. Orton, Jr., and W. Stout have kindly given the author much information regarding the shale formations of the State.

[2] Ohio Geol. Surv., Vol. VII, Pt. I, p. 56.

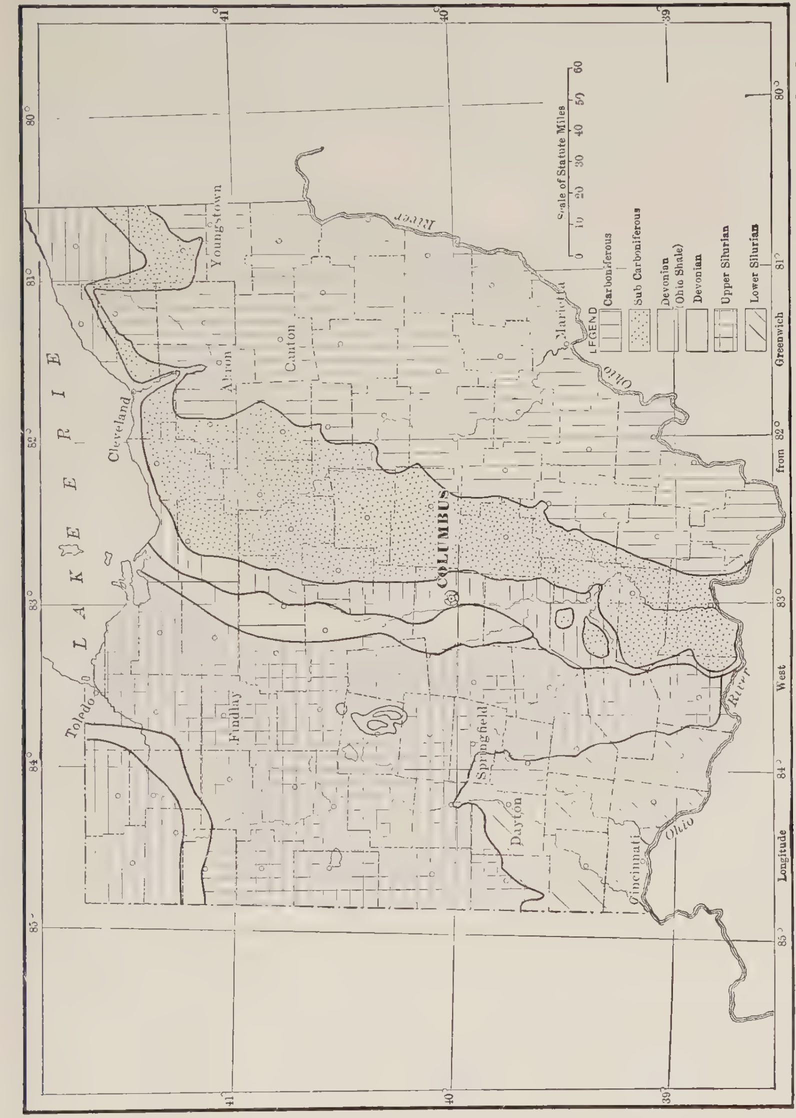

FIG. 149.—Map of Ohio, showing distribution of clay- and shale-bearing formations. After Orton, Geology of Ohio, VI, 1888.)

hollow blocks, and fireproofing. At Taylor Station near Columbus, the shale is employed for face brick, common brick, hollow blocks and drain-tile. At Junction City, Perry County, paving-brick and hollow bricks are made from it, while at Hanover, Licking County, and Wooster, Wayne County, it is employed for face brick.

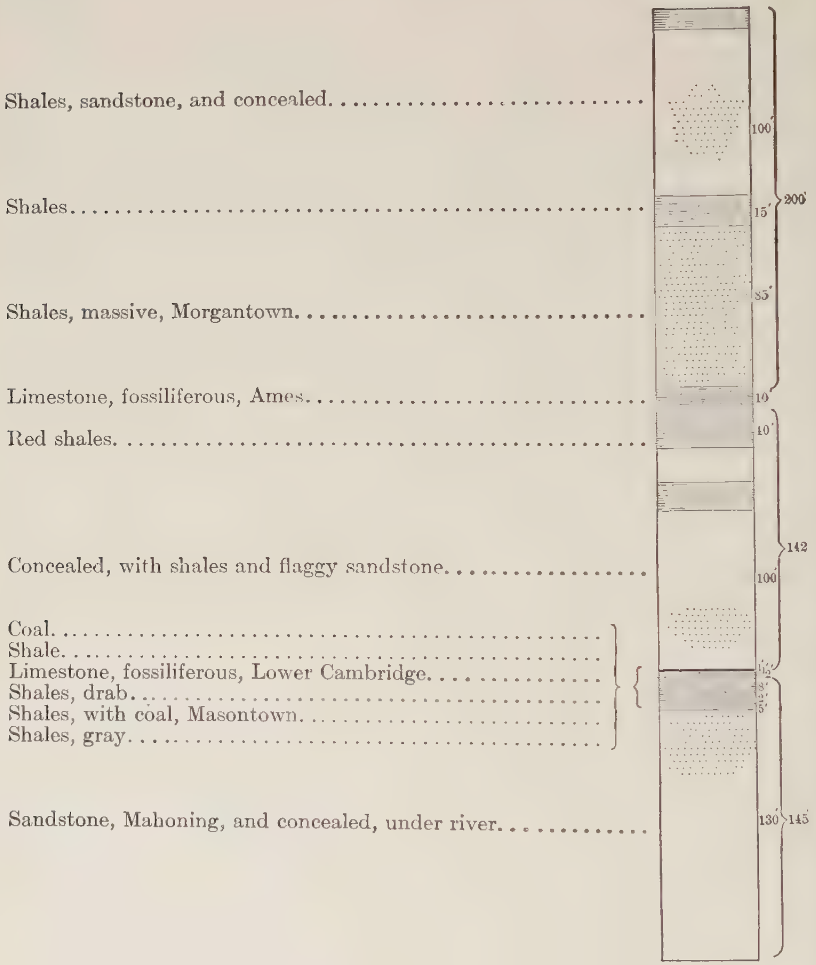
Shales, sandstone, and concealed
Shales
Shales, massive, Morgantown
Limestone, fossiliferous, Ames
Red shales
Concealed, with shales and flaggy sandstone
Coal
Shale
Limestone, fossiliferous, Lower Cambridge
Shales, drab
Shales, with coal, Masontown
Shales, gray
Sandstone, Mahoning, and concealed, under river
100'
15'
200'
85'
10'
10'
142
100'
8'
5'
130'
145'

FIG. 150.—Section of Barren Measures opposite Steubenville, Ohio. (After White, U. S. Geol. Surv., Bull. 65, p. 77, 1891.)

The Logan shale, occurring in the lower part of the Logan formation, is now extensively used.

PENNSYLVANIAN [1]

The formations of the Pennsylvanian underlie the eastern third of the State. The lower members are found in the western and southern portions of the area, while the upper members underlie the surface in the middle part of the area and towards the Pennsylvania border. The Pennsylvanian formations include the best clays in the State, and both shales and clays are numerous throughout the series.

The shales of the Pottsville and Allegheny series are among the most widely used in Ohio, the products made from them including face brick, paving-brick, sewer-pipe, hollow brick, and radial blocks.

Roofing-tile are made at New Lexington from a shale overlying the Brookville coal; at Akron from one near the horizon of the Quakertown or No. 2 coal; and at East Sparta from a deposit over the No. 4 coal of the Allegheny series.

Pottsville series.—The clays found in the Pottsville, together with brief reference to their characters, are noted below, beginning with the lowest one (Ref. 7):

Sharon.—A clay of rather patchy occurrence, siliceous character and not used. The Sharon shales, which overlie the Sharon coal, have been extensively used for sewer-pipe.

Sciotoville.—The most refractory clay found in Ohio. It carries flint, semi-flint, plastic and some " pink-eye " clay (a mottled, semi-refractory plastic clay). The beds are not persistent, and the best occurrences are in Scioto County. It is used for refractory wares, and when mixed with shale, for paving-brick as in the Portsmouth district.

Huckleberry.—Of local occurrence, little used, and of only moderate refractoriness.

Quakertown.—Best developed in southern Ohio. Siliceous, plastic, and of low refractoriness. Not used.

Bear Run.—Unimportant.

Vandusen.—Unimportant.

Lower Mercer.—A siliceous plastic clay of moderate refractoriness, which is thin and uncertain as well as lacking in persistence.

Middle Mercer and Flint Ridge.—Mostly a siliceous, plastic clay, with some flint-clay. It is rated as third in importance of the Ohio Pottsville clays. The members extend across the State from Scioto to Mahoning County, but the areas of most importance are in Perry, Muskingum, and Summit counties. These clays make good stoneware, but are little used for this purpose. They also make a fine gray building-brick. In addition they work well for sewer-pipe, fireproofing, conduits, buff building-brick, and common fire-brick. They are somewhat low in refractoriness.

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[1] For detailed discussion of the Pennsylvanian fire-clays see Ref. 7.

Upper Mercer.—Best developed in southern Ohio from Vinton County to the Ohio River. Mostly plastic. Has been worked for face brick and second grade fire-brick.

Bedford.—A plastic siliceous clay used only at Dalton for stoneware.

Tionesta or Mount Savage Clay.—The most important clay in the Pottsville of Ohio. It has a wide distribution from Scioto and Lawrence counties on the south to Mahoning and Columbiana counties on the north. The main body of the material is always plastic, but occasionally flint-clay and pink-eye are found. Its fusion-point averages from cone 20 to 23. This clay has a wide range of uses from brick to art pottery, but for most purposes it is not used alone. The products also include sewer-pipe, saggers, wall-coping, floor-tile, flue-lining, stoneware, etc.

Brookville.—Mostly a plastic siliceous clay with an average thickness of 6 feet, and forming a great reserve supply. It is worked chiefly in Tuscarawas and Stark counties, but is also well developed in Muskingum, Coshocton, Holmes, and Wayne counties. Its chief use is for high-grade building-bricks and blocks, but mixed with other clays it works well for stoneware and allied products.

Allegheny series.—*Winters clay.*—Of little importance.

Clarion.—Of value in southern and eastern Ohio. Carries both plastic- and flint-clay, but the latter is only of local occurrence. It is used for a variety of refractory and hollow-ware products, as fire-brick, sewer-pipe, segment block, flue-lining, wall-coping, and building-block. It was formerly used for stoneware and yellow ware.

Lower Kittanning.—This is the great clay horizon of the State. Its thickness ranges from 2 to 20 feet with an average of 8 feet. The clay is mostly plastic, but locally may carry flint-clay. The main districts of development are along the Tuscarawas Valley, in Tuscarawas County, the Ohio Valley in Columbiana and Jefferson counties, and the Hocking Valley in Athens and Hocking counties. The clay is used most extensively for sewer-pipe, fire-proofing, and allied products; also in the manufacture of fire-brick, and in mixtures for stoneware and yellow ware. Some building and paving-brick are also made from it.

Oak Hill.—Discontinuous. Chiefly of value in Jackson County. It carries both flint- and plastic-clay, and is used for refractory ware.

Middle Kittanning. Forms a persistent bed across the State, from Lawrence to Columbiana County. It is plastic, but of variable quality and lacks in refractoriness. Is largely used for fireproofing, building-block, paving- and face-brick.

Lower Freeport.—Unimportant.

Bolivar.—This clay is often absent, and is little used. It may carry both plastic- and flint-clay.

Upper Freeport.—A rather persistent clay, of variable character and thickness, which is plastic and usually siliceous. It is not very refractory, and of minor importance, but is used for sewer-pipe mixed with Mahoning clay.

Conemaugh series.—The Conemaugh shales are not used for paving-brick, but are employed for building-brick and hollow tile. The shale under the Pittsburg coal is worked at Bellaire for building-brick and hollow blocks.

The clays found in the Conemaugh, beginning at the bottom of the series, are as follows:

Mahoning or *Thornton clay.*—This is 1 to 10 feet thick, plastic, of variable character and low refractoriness. It is of little importance, but is used at Dennison, Tuscarawas County, for sewer-pipe, flue-linings, wall-coping, etc.

Mason.—A plastic, siliceous, sometimes shaly clay, rarely over 3 feet thick, and not used.

Wilgus.—Low grade, thin and uncertain. Not used.

Anderson.—A plastic clay, non-refractory and often impure.

Averages 7 feet in thickness. Not used.

Barton.—No importance. Irregular, and not used.

Harlem.—Too thin and impure for use.

Pittsburg.—Widely distributed, but of small value, due to thinness and objectionable impurities.

Monongahela series.—This contains several clays, but they are unimportant, and hold little promise.

Dunkard or Upper Barren Measures.—In Ohio these underlie an area extending through the counties of Belmont, Monroe, Washington, Athens, Meigs, and Gallia.

Pleistocene

Pleistocene clays are found in all parts of the State, but they are used chiefly for common brick and drain-tile.

TESTS AND ANALYSES OF OHIO CLAYS

The following tests and analyses are taken from the Ohio State Geological Survey reports:

ANALYSES OF OHIO CLAYS

	I.	II.	III.	IV.	V.	VI.	VII.
Silica (SiO_2)	76.24	63.09	52.52	61.86	69.37	69.79	56.44
Alumina (Al_2O_3)	16.87	20.17	31.84	26.02	19.08	19.31	26.60
Ferric oxide (Fe_2O_3)	0.16	2.12	0.67	0.63	1.26	......	2.00
Lime (CaO)	0.50	......	0.50	1.26	0.60	......	0.47
Magnesia (MgO)	trace	......	0.19	0.19	0.63	......	0.63
Potash (K_2O)	1.09	2.76	0.59	0.31	2.14	......	3.20
Soda (Na_2O)			....		0.02	......	0.26
Water (H_2O)	5.14	5.41	11.68	9.73	5.57	5.09	7.57
Moisture		6.45	0.69	......	0.94	1.02	2.48
Titanium oxide (TiO_2)	......	......	1.68	......	0.29		

	VIII.	IX.	X.	XI.	XII.	XIII.	XIV.
Silica (SiO_2)	68.13	66.21	57.15	57.10	49.30	58.20	57.28
Alumina (Al_2O_3)	20.80	21.13	20.26	21.29	24.00	22.47	21.13
Ferric oxide (Fe_2O_3)	1.20	1.28	7.54	7.31	8.40	5.63	8.52
Lime (CaO)	0.42	0.51	0.90	0.29	0.56	0.62	5.79
Magnesia (MgO)	0.37	0.18	1.62	1.53	1.60	0.98	2.13
Potash (K_2O)	2.28	1.42	3.05	3.44	3.91	3.08	
Soda (Na_2O)	0.27	0.38	0.58	0.61	0.19	0.42	
Water (H_2O)	5.72	6.29	5.50	6.00	9.40	6.15	5.22
Moisture	1.00	1.65	2.70	1.30	1.20	1.65	
Titanium oxide (TiO_2)							

	XV.	XVI.	XVII.	XVIII.	XIX.	XX.
Silica (SiO_2)	52.19	53.38	44.60	59.92	57.80	51.72
Alumina (Al_2O_3)	14.61	19.36	40.05	27.56	25.54	30.10
Ferric oxide (Fe_2O_3)	10.00	14.86	0.80	1.03	2.51	1.94
Lime (CaO)	......	1.48	0.27	trace	0.25	0.62
Magnesia (MgO)	......	1.06	trace	trace	0.61	0.53
Potash (K_2O)	......	......	trace	0.67	2.51	2.74
Soda (Na_2O)	......	......	trace	......	0.18	
Water (H_2O)	5.62	......	14.23	9.70	8.35	9.95
Moisture	12.62	......	......	1.12	2.25	1.05
Titanium oxide (TiO_2)	......	......	......	......	......	1.35

LOCALITIES OF THE ABOVE

No.	Locality.	Geological Age.	Uses.
I.	Haydenville.	Lower Carboniferous.	Fire-brick
II.	North Industry.	Lower Coal-measures.	Paving-brick
III.	Mineral Point.	Lower Kittanning.	Refractory wares
IV.	Darlington.	“ “	Paving-brick
V.	Roseville.		Stoneware
VI.	Roseville.		Cooking ware
VII.	Steubenville.		Stoneware
VIII.	Akron.	Lower Carboniferous.	Stoneware
IX.	Zanesville.	Lower Coal-measures.	Cooking ware
X.	Gloucester.	Cambridge.	
XI.	Canton.	Lower Coal-measures.	Paving-brick
XII.	Waynesburg.	Middle Kittanning.	Brick
XIII.	Zanesville.	Freeport shale. . . . . Kittanning clay.	
XIV.	Northern Ohio.	Bedford shale.	Paving-brick
XV.	North Industry.	Lower Carboniferous.	Paving-brick
XVI.	Canton.	“ “	
XVII.	Scioto County.	“ “	Fire-brick
XVIII.	Salineville.		Fire-brick
XIX.	East Palestine.	Upper Freeport.	Paving-brick
XX.	Jefferson County. . . .		Sewer-pipe

Nos. I–XX from Ohio Geol. Surv., VII, 1893.

ANALYSES OF COAL MEASURE CLAYS

	I	II	III	IV	V
SiO_2.	45.13	64.60	60.00	54.33	59.55
Al_2O_3.	34.08	18.98	22.37	27.01	24.28
Fe_2O_3.	2.35	3.43	2.68	2.38	2.38
CaO.	.25	.15	.41	.20	.32
MgO.	.54	.87	.13	.05	.88
TiO_2.	2.08	1.35	1.65	1.98	1.56
P_2O_5.	.11	.02	.01	.03	.12
Na_2O.	.62	.21	.31	.18	.09
K_2O.	.76	3.16	2.59	1.46	1.91
MnO.	.01	.02	.01	Tr.	Tr.
S.	.17	.02	.02	.05	.07
Total C.	.52	.38	.30	.48	.22
Inorganic carbon	.00	.06	.03	.03	.01
Loss 105° C. . . .	1.62	1.26	2.83	2.60	1.75
Ignition loss. . . .	12.76	5.79	6.30	9.33	7.74

For localities of the above see table of physical tests following:

	I	II	III	IV	V
Water of Plasticity	13.70	22.74	21.81	23.48	24.50
Drying linear shrinkage	3.75	4.60	6.65	5.96	7.15
Drying volume shrinkage	11.67	14.43	21.25	18.92	23.01
Burning tests, volume shrinkage:					
Cone 2	....	15.06	14.29	13.31	15.93
Cone 7	17.94	17.26	19.36†	20.15†	19.11
Cone 14	16.67	3.15*	3.87*	20.57	1.75
Absorption:					
Cone 4	....	16.59	16.74	22.53	17.48
Cone 7	17.08	0.6	2.24†	11.78†	6.94
Cone 14	17.45	0.45*	1.31	0.59	0.86
Deformation cone	32½	17	23	29	27

* Cone 12. † Cone 6.

I. Sciotoville flint clay, Edmonds, Scioto County.
II. Flint Ridge plastic clay, McArthur, Jackson County.
III. Tionesta clay, Roseville, Perry County.
IV. Clarion clay, Hamden, Vinton County.
V. Lower Kittanning clay, Eifort, Scioto County.
Numbers I–V from Ohio Geol. Surv., 4th ser., Bull. 26, 1923.

REFERENCES ON OHIO CLAYS

1. Lovejoy, E., Notes on Fire-clays of the Northern Appalachian Coal Basin, Jour. Amer. Ceram. Soc., Vol. II, p. 374, 1919.
2. Orton, E., The Clays of Ohio, Their Origin, Composition, and Varieties, Ohio Geol. Surv., Vol. VII, p. 45, 1893.
3. Orton, E., Jr., The Clayworking Industries of Ohio, Ohio Geol. Surv., Vol. VII, p. 69, 1893.
4. Prosser, C. S., Geological Scale of Ohio, Ohio Geol. Surv., 4th ser., Bull. 7, 1905.
5. Stevenson, J. J., Carboniferous of the Appalachian Basin, Bull. Geol. Soc. Amer., Vol. XV, p. 37, 1904.
6. Stout, W., Geology of Southern Ohio, Ohio Geol. Surv., 4th ser., Bull. 20, 1916.
7. Stout, W., Stull, R. T., McCaughey, W. J., Demorest, D. J., Coal Formation Clays of Ohio, Ohio Geol. Surv., 4th ser., Bull. 26, 1923.
8. Stout, W., The Flint Clay Situation in Ohio, Jour. Amer. Ceram. Soc., Vol. VI, p. 1153, 1923.
9. Van Horn, F. B., Clay and Shale Resources in the Vicinity of Cleveland, Ohio, Trans. Amer. Ceram. Soc., Vol. XVIII, p. 450, 1916.

OKLAHOMA

Clay-bearing formations.—Clays or shales occur in beds of the Ordovician, Devonian, Mississippian, Pennsylvania, Permian, and Cretaceous.

Ordovician

Shales of Ordovician age outcrop in the Arbuckle Mountains, Ouachita and Ozark Mountains regions, but little is known of their properties or availability for use. The outcrops are in thinly settled country with poor transportation facilities.

Devonian

The Chattanooga formation outcropping in the Ozark region in the northeastern corner of the State, is the only argillaceous one of Devonian age. It is hard and siliceous, as well as containing bituminous material, so that it may be of little value unless weathered. No use has been made of it.

Mississippian

The Caney shale, 1500 to 1600 feet thick, outcrops in the Arbuckle Mountain region, but is probably not of much value. Another one is found in the Fayetteville formation also in the northeastern part of the State, but this, too, has not been tested. A third, the Standley, is found in the Ouachita Mountains, and while it contains a number of sandstone beds, the shale seems to have good working qualities and is red-burning.

Pennsylvanian

The area underlain by these formations includes approximately that part of the State north of the Arbuckle and Ouachita Mountains, west of the Grand River, and east of the Red Beds. It contains the best clay deposits of the State. Their development has been aided by cheap local fuel. While the formation names are different for the areas north and south of the Arkansas River four group names, Muskogee, Tulsa, Sapulpa, and Ralston, are recognized in both areas.

The Muskogee group north of the Arkansas River has one important shale-bearing formation, the Vinita, which outcrops in a crescent-shaped area around the Ozark uplift. Both the fresh and weathered shale are used for common brick, sidewalk brick, and drain-tile.

South of the Arkansas River the Muskogee has several shales. Of these the Atoka could probably be used for brick and drain-tile. The McAlester which carries the coal-beds yields a blue shale used for paving- and building-brick. Other shales are the Winslow, Savanna, Boggy, and Senora, which are red-burning and are used for common and paving-brick. No fire-clays have been found.

In the Tulsa group the shales north of the Arkansas River are the most valuable, and are worked at several localities for building- and paving-brick. South of the river the Tulsa carries blue and brown shales which are used at only one plant.

The Sapulpa group contains a great thickness of shale and red sandstone, the former being red-burning, and used for common, front and paving-brick, as at Bartlesville, Tulsa, etc.

Red Beds

The Red Beds of the Permian and Pennsylvanian are the surface formations in the western half of the State. The shales are chiefly red, and interstratified with clayey sandstone. Some are too gypsiferous for use. The better ones are worked at a number of localities for brick manufacture.

Cretaceous and Tertiary

The principal area of Cretaceous rocks is in the extreme southern portion of the Arbuckle and Ouachita Mountains. The Bokchito formation of the Cretaceous contains red-burning shale, but it has not been developed.

Nothing is known regarding the Tertiary clays which are found in the northwest corner of the State.

The following physical tests are from the Oklahoma Geological Survey report (Ref. 1):

Physical Tests of Oklahoma Clays

	I	II	III	IV
Water of plasticity, per cent	21.8	20.4	19.4	23.1
Drying shrinkage, per cent (linear)	6.8	7.6	7.2	9.6
Fire shrinkage, per cent (linear)	8.9	7.9		
Porosity:				
Cone 010	....	....	....	24.1
Cone 06	19.0	14.5	23.3	7.8
Cone 04	9.2	6.8	24.0	9.9
Cone 02	3.3	6.2	15.3	2.7
Cone 1	4.5	3.6	6.2	2.0

I. Muskogee, Okla.
II. Cleveland, Okla.
III. Oklahoma City, Okla.
IV. McAlester, Okla.

REFERENCES ON OKLAHOMA CLAYS

1. Shannon, C. W., Clays of Oklahoma, Okla. Geol. Surv., Bull. 22, p. 118–121, 1914.
2. Snider, L. C., Preliminary Report on the Clays and Clay Industries of Oklahoma, Okla. Geol. Surv., Bull. 7, 1911.

OREGON

Little has been published regarding the clay resources of this State, but it is known that the clay-bearing formations range from Jurassic to Recent in geologic age. There are also some residual clays from basalt. Most of the clays worked are either of Eocene age or Recent alluvium. The main development has been in the western part of the State especially near Portland. There are few brick-plants in the rest of the State.

Eocene

The main belt of clay-bearing rocks of this formation runs north and south along the eastern slope of the Coast Range. It is said to yield white, buff and red-burning plastic clays in pockety deposits which are more or less intermixed. No high-grade clays have been found. Common and face-brick, drain-tile and fireproofing are the chief clay products.

Alluvial Clays

These are red-burning surface clays and loams which are found chiefly in the river valleys.

Residual Clays

Residual clays from basalt are worked for common brick by some of the yards at Portland.

REFERENCES ON OREGON CLAYS

1. Geijsbeek, S., The Clay Deposits of Oregon, Trans. Amer. Ceram. Soc., Vol. XV, p. 644–658, 1913.
2. Parks, H. M., The Economic Geological Resources of Oregon, Ore. State Bur. Mines (Ore. Agric. Coll. Bull., Extens. Ser. 5, No. 2), 1912.

PENNSYLVANIA[1]

The geologic formations of Pennsylvania range from the pre-Cambrian crystalline rocks to those of Pleistocene age.

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[1] Dr. G. H. Ashley and Mr. R. W. Stone have supplied much recent information regarding the Pennsylvania clays.

In the western part of the State, except the northwestern counties the rocks are nearly all of Carboniferous age, the beds being bent into a series of gentle folds; but often the exposure of the lower or older beds is due partly to the overlying strata having been worn away.

To the eastward the rocks become highly folded in the central counties of the State, so that the strata often have a very high pitch. This folding has raised the strata so that rocks of Carboniferous age have been removed from all of the area east of the Allegheny Front except in the Broad-Top and anthracite coal fields. The folding, however, exposes the underlying Devonian, and lower rocks down to the middle of the Cambrian. Rocks of the several ages lie in bands which extend in a general northeast-southwest direction. Toward the southeast corner of the State the underlying basal Cambrian and pre-Cambrian rocks are exposed.

On the eastern edge of the State there is a fringe of coastal-plain formations, but with the exception of certain loams, they have little value in Pennsylvania. North of the terminal moraine the drift-clays are widespread.

Residual Clays

These might occur at almost any point in the area lying south of the terminal moraine, but the deposits of greatest economic value are those found in the Great Valley, along the line of which, as well as in the South Mountain region, Fig. 151, there are a number of deposits of white and variegated clays.

Those in the South Mountain region have been derived from the decomposition of hydromica slates, which are interstratified with Ordovician limestones and quartzites, talcose slates, and limestones of Cambrian age. Of recent years these white clays have been much worked for paper manufacture, and to a less extent for tile, fire-brick, and Portland cement.

In the Saylorsburg district of eastern Pennsylvania (Ref. 25) there is a series of deposits of whitish residual clay formed by the weathering of calcareous sandy shales and cherty limestones, which underlie the Oriskany sandstone. The clay has been worked by shafts. Some of it has been washed and used as filler, while the crude material has been employed in Portland cement manufacture. (Ref. 15, 18.)

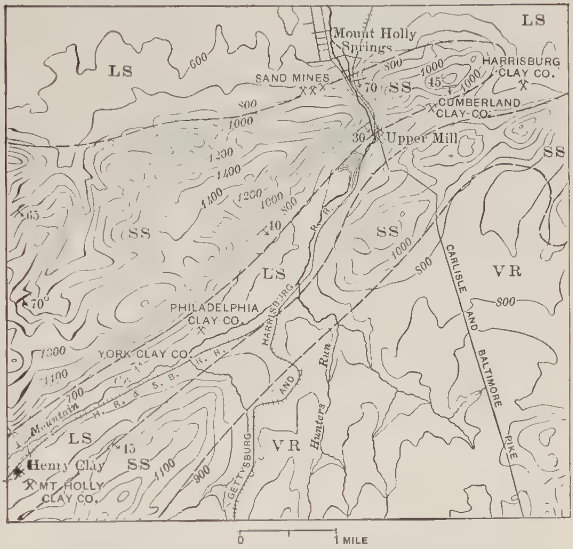
Residual clay from the contact of Ordovician limestone and Cambrian sandstone, was formerly worked near Glen Loch, Delaware County (Refs. 11, 18). Other deposits of the same age have been worked near Narvon, Lancaster County (Ref. 18).

In Central Pennsylvania, chiefly in the Nittanny Valley, the Upper Cambrian has yielded a number of deposits of white residual clays in

Center, Huntingdon, and Blair counties. Their chief use has been in steel works (Ref. 14, 18).

A number of localities are mentioned in reports of the Second Geological Survey,[1] but many of these are no longer worked. Later many of these were described in detail by T. C. Hopkins (Ref. 10–12). More recently the Topographic and Geologic Survey of Pennsylvania has issued bulletins on deposits in Monroe and Blair counties.[2]

A second type of white residual clay or kaolins are those of Delaware and Chester counties, which have been formed by the weathering of pegmatites. These have been worked near Kaolin P. O., Brandywine Summit, etc., but working has ceased in recent years because the deposits, being the product of weathering, have in some cases been exhausted with depth.



VR, pre-Cambrian volcanic rocks; SS, Cambrian sandstone and shale, LS, Cambrian limestone

FIG. 151.—Map of South Mountain region, Pa., showing distribution of clays. (After Stose, U. S. Geol. Surv., Bull. 315, 1907.)

DEVONIAN, SILURIAN, AND ORDOVICIAN SHALES

The vast beds of shale occurring in these systems in the eastern and south-central portions of Pennsylvania afford an excellent field for exploitation by the clay-worker.

The Devonian is found underlying large areas in northwestern Pennsylvania and may be of value, but in the northeastern counties the beds are often too siliceous.

To the south and southeast shales of Devonian, Silurian, and Ordovician age appear as a series of bands in Lackawanna, Luzerne, Carbon,

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[1] Second Pa. Geol. Surv., Rept. C4, pp. 137, 272, 275, 277, 279, 325, 340, and Rept. CC, p. 203.

[2] Penna. Top. and Geol. Surv., Bulls. 40 and 45, 1922.

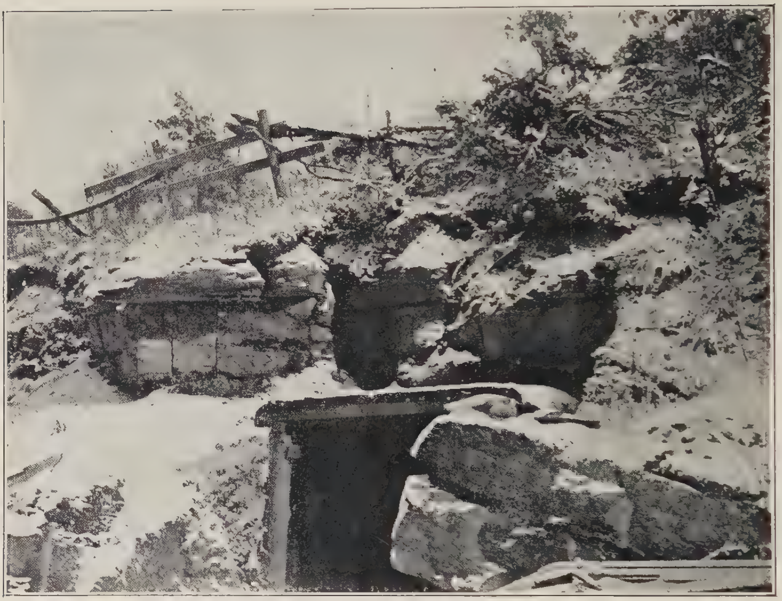

FIG. 152.—Fire-clay underlying Lower Mercer limestone, Union Furnace, O. (Photo by B. S. Fisher.)

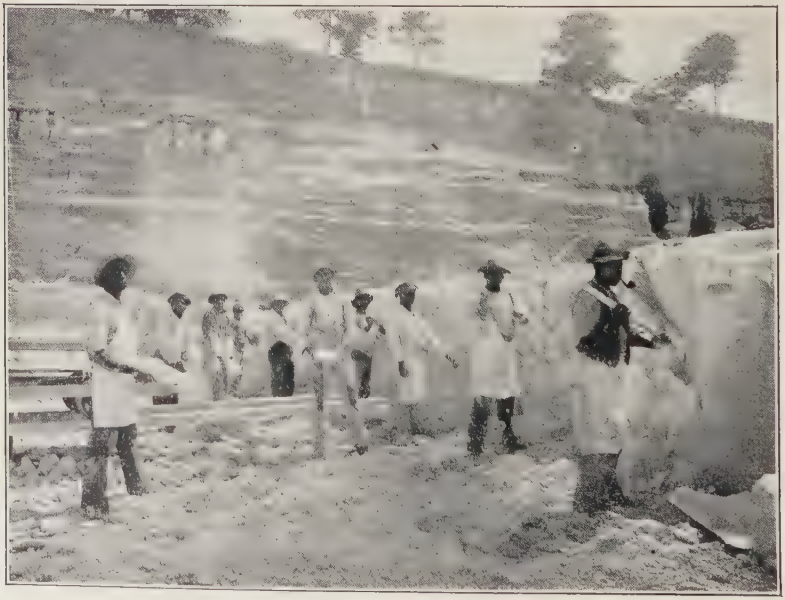

FIG. 153.—White sedimentary clay, Aiken area, S. C. (After Sloane, S. C. Geol. Surv., Bull. 1, 1904.)

Cumberland, Snyder, Juniata, Perry, and other counties, and are worked at several localities for the manufacture of both building- and paving-brick. The Clinton shales have been dug for brick-making in Laurelton and Hartleton townships of Union County and at Watsontown, east of Williamsport; and the Martinsburg shales at Reading and Harrisburg.

CARBONIFEROUS

To the clay-worker the most important group of formations occurring in Pennsylvania is of Carboniferous age. It includes a wide range of plastic materials from sandy shales up to the highest grades of fire-clay. Unfortunately, detailed systematic study of the shales and fire-clays of the entire Carboniferous area of Pennsylvania has but recently been undertaken, so that at present only scattered references are available. These occur in the reports of the Second Geological Survey of Pennsylvania, reports of Hopkins in western Pennsylvania, and a paper by Ashley before the Ceramic Society of America,[1] and brief references in recent publications of the Topographic and Geologic Survey of Pennsylvania. Various references are found on p. 538. The occurrences are here taken up in regular order beginning with the oldest.

Mauch Chunk.—Shales of this age have been worked for bricks at Kane and Hazleton.

Pottsville.—This part of the Carboniferous is composed chiefly of sandy beds, as sandstone and conglomerates, but contains several beds of shale and coal, the latter usually underlain by fire clay. The most important of these clays is thought to belong in the position of the Mercer coal. The Upper Mercer coal is underlain by a fire-clay in Elk, Butler, Huntingdon, McKean, and Cameron counties, while in Beaver, Lawrence, and Mercer counties shale beds have been noticed in this position, but no fire-clays. Plastic clay is also recorded from Mayport, Clarion County (Ref. 13); and flint-clay from Climax and St. Charles, Armstrong County (Ref. 3). The principal deposits, however, lie in the central part of the State particularly in Clearfield, Centre, Clinton, Cameron, and Elk counties.

In Elk County a bed of fire-clay, said to be associated with an Alton coal-bed, has been worked in Benezette township. Another bed below the Mercer is found in Mercer County.

Flint-clays assigned to the Mercer horizon, are or have been mined extensively in Clearfield County at Lumber City, Curwensville, Mineral Spring, Woodland, Bigler, Wallaceton, West Decatur, Burly, Chase, Faunce; at Sandy Ridge, Orviston, and Hayes Run, Centre County; Queens Run, Farrandsville, and on Tangascootack Creek, in Clinton County.

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[1] Ashley, George H., The Fire Brick Materials of Pennsylvania, Jour. Amer. Ceram. Society, Vol. 6, No. 7, July, 1923.

Clay at the Mercer horizon has long been mined extensively on the western flank of Chestnut Ridge in Fayette and Westmoreland counties, and at Keystone in Somerset County. Good clay is confined to the zone of weathering. Iron has been brought together here in the form of nodules which are easily separated.

Allegheny Group or Lower Productive Measures.—This group contains a number of important beds of fire-clay and coal in western and western-central Pennsylvania. The group rests on the Pottsville sandstone, and extends to the top of the Upper Freeport coal. Along the upper Ohio River, where the section is specially important, the following beds are seen:[1]

SECTION ALONG THE UPPER OHIO RIVER IN PENNSYLVANIA

1.	Upper Freeport coal; "Four-foot "or "Hookstown vein"	0 to 4	180
2.	Fire clay	2 to 4	
3.	Limestone	1 to 4	
4. 5.	Shale and Sandstone	50 to 70	
6.	Lower Freeport coal (usually absent)	0 to 2	
7.	Fire clay	0 to 5	
8.	Limestone (sometimes present)		
9.	Sandstone, or sandstone and shale	70 to 90	
10.	Darlington; "Block vein" at Smith's Ferry	1 to 2	
11.	Fire clay	4	
12.	Black slate with iron nodules	20 to 30	
13.	Lower Kittanning coal; "Sulphur vein"	2 to 3	
14.	Fire clay	6 to 10	
15. 16.	Sandstone Shale	40	
17.	Limestone, ferriferous, "Vanport limestone"	1 to 20	100
	Black shale	15	
18.	Fire clay Sandy shale Fire clay	20	
19.	Clarion coal	1±	
20.	Fire clay	4 to 6	
21.	Sandstone	23	
22.	Shale	25	
23.	Brookville coal	6	
24.	Fire clay	4	

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[1] U. S. Geol. Surv., Bull. 225, p. 467, 1904.

Brookville clay.—The Brookville coal is underlain by a persistent bed of clay. In parts of western Pennsylvania some at least of the flint-clay ascribed to the Mercer horizon may belong at or near the horizon of the Brookville coal. In the upper Ohio and Beaver River region this clay is irregular and often impure.[1]

Clarion flint-clay.—Flint-clay occurs in Clarion County and elsewhere between the Lower Kittanning coal and the Vanport limestone. It has been mined at Bolivar for fire-brick,[2] and has also been mined on Brady's Run, Beaver County.

It has been extensively mined in Clearfield County at Woodland, Krebs, and elsewhere, and at many points in Clarion County.[3] It is usually described by the clay men as differing from the Mercer clay in quality and in lack of persistence, as a clay showing a good thickness on the outcrop but turning into soft clay on driving under the hill. Clays and shales of the Clarion member of the Allegheny group are mined for brick-making, notably at Clearfield, Kittanning, and at many other places.

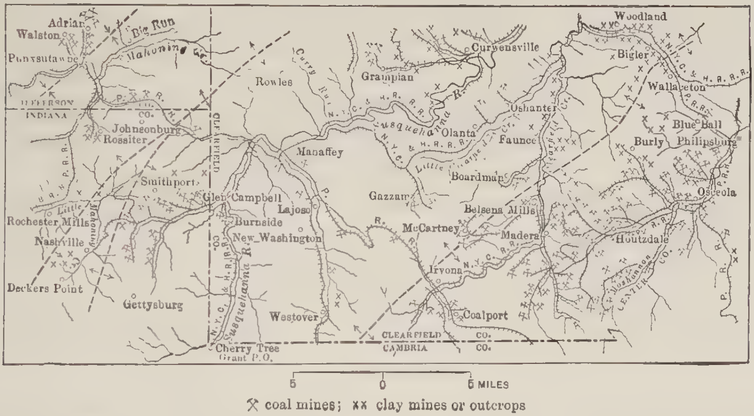

FIG. 154.—Map of South Clearfield and parts of Indiana and Jefferson counties, Pa. (After Ashley, U. S. Geol. Surv., Bull. 285, 1906.)

Lower Kittanning clay.—Underlying the Lower Kittanning coal there is an important bed of clay which is often more valuable than the coal, and has been extensively used for the manufacture of clay products. So commonly is the Lower Kittanning coal underlain by the thick under-clay that this character has been used by the geologists as one means of identifying that coal-bed. In places the clay reaches a thickness of 20 feet or more. It has been extensively developed along Beaver River and westward from there down the Ohio. It is much used by the pottery and tile works at New Brighton, East Liverpool, etc.

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[1] Hice, R. R., Trans. Amer. Ceram. Soc., Vol. VII, Pt. II, p. 251.

[2] Second Penn. Geol., Rept. K3, p. 43.

[3] Clays of the Clarion Quadrangle, E. F. Lines, Bull. 315, pp. 335 to 343, 1907.

Hice[1] states that in the upper Ohio and Beaver River region it is persistent, quite constant in quality, and has a good roof, but on account of the extent to which it has been worked in this area it is sometimes called the "New Brighton clay." Pottery, hollow ware, fire-brick and paving-brick have all been made in Beaver County from this clay, different parts of the deposit being used for these several purposes, either alone or mixed with other clays.

The sections given in Fig. 156 represents the position of the Lower Kittanning clay at several localities. The Second Pennsylvania Geological Survey reports refer to it in the counties of Armstrong,[2] Beaver,[3] Fayette, and Westmoreland.[4]

Stoneware clay at this horizon is reported from Girty,[5] a flint-clay from the Little Mahoning Creek drainage basin of central Pennsylvania (Fig. 154) (Ref. 2); plastic clay from Clarion County (Ref. 13); and a persistent bed of flint-clay of variable quality in the northern half of the Kittanning and Rural Valley quadrangles (Ref. 3).

Middle Kittanning clay.—This bed (known locally in Beaver County as the Darlington) is commonly found under the coal of the same name in Allegheny, Armstrong, Tioga, Blair, and Beaver counties. It is being worked in Beaver County on Brady's Run, and is there partly a flint-clay. The clay is not uniform in thickness, and of more variable quality than the Lower Kittanning.

Woolsey[6] states that in the Ohio Valley the bed is a very persistent one, but rarely worked on account of the iron nodules which it contains.

Ashley (Ref. 2) reports a flint-clay at this horizon at a number of widely separated points in central Pennsylvania, especially about Westover and near McCartney in Clearfield County. It is worked for stoneware at Hawthorne, Clarion County (Ref. 13).

Upper Kittanning clay.—Clay under the Upper Kittanning coal appears to be rarely of value in Pennsylvania.

Lower Freeport clay.—Above the Kittanning member of the Allegheny comes the Freeport member containing two coals and underlying clays, and two limestones which underlie the clays.

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[1] l. c.

[2] H5. See also Hopkins, Clays of Western Pennsylvania, Ann. Rept., Pa. State College, 1897, p. 33.

[3] Q., p. 58, 59, 190, 193, 195, 205 and 215.

[4] K3., p. 40.

[5] U. S. Geol. Atlas, Folio, Elders Ridge, No. 123.

[6] l. c., p. 472.

The Lower Freeport clay does not appear to have assumed much importance, and little mention is made of it in print. In the upper Ohio and Beaver River region it is generally quite thin, but in places reaches a workable thickness, and at one point on Brady's Run 22 feet have been mined. It has been used for low-grade fire-brick, but usually carries too many impurities to allow its use for refractory purposes. It is generally thoroughly vitrified at cones 6 and 7.[1] On Block House Run, Beaver County, it has been worked for sewer-pipe.[2] It has been used also in Armstrong County.

Upper Freeport limestone clay or Bolivar fire-clay.—A short distance under the Upper Freeport coal and associated with the Upper Freeport limestone, though often present when the limestone is absent, is found a bed of high-grade fire-clay known as the Bolivar clay, long mined at the locality of that name in Westmoreland County. It is a non-plastic or flint-clay, which has been extensively used in fire-brick manufacture. On the Ohio and Beaver rivers this seems to be replaced by a less refractory shale. Flint-clay, usually too ferruginous for high refractory ware, is found at many points in central and western Pennsylvania at this horizon. In places the flint-clay and soft clay appear to be intimately associated, in others they are distinctly separated, the flint-clay underlying the soft clay.

Upper Freeport clay.—This underlies the Upper Freeport coal, but is often more persistent than its coal-bed. In the Ohio Valley region it is found at several points,[3] and has been used for fire-brick. It is sometimes mixed with the Lower Kittanning clay. It has also been worked around Bolivar and Salina. As a rule this clay almost equals the clay under the Lower Kittanning coal in thickness, if not in value.

Conemaugh group or "Lower Barren Measures."—These consist largely of shales and sandstones with some limestones, the shales predominating in the upper part of the section and the sandstones in the lower. They extend from the Upper Freeport coal to the base of the Pittsburgh coal, and their general character can be well seen from the accompanying section (Fig. 157). They form the surface of a large area in Allegheny, Armstrong, Butler, Beaver, and Westmoreland counties.[4]

Their importance was well set forth in a report issued by the Penn-

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[1] Hice, l. c.

[2] Woolsey, l.c., p. 472.

[3] Woolsey, l. c., p. 472.

[4] See map, U. S. Geol. Surv., Bull. 65.

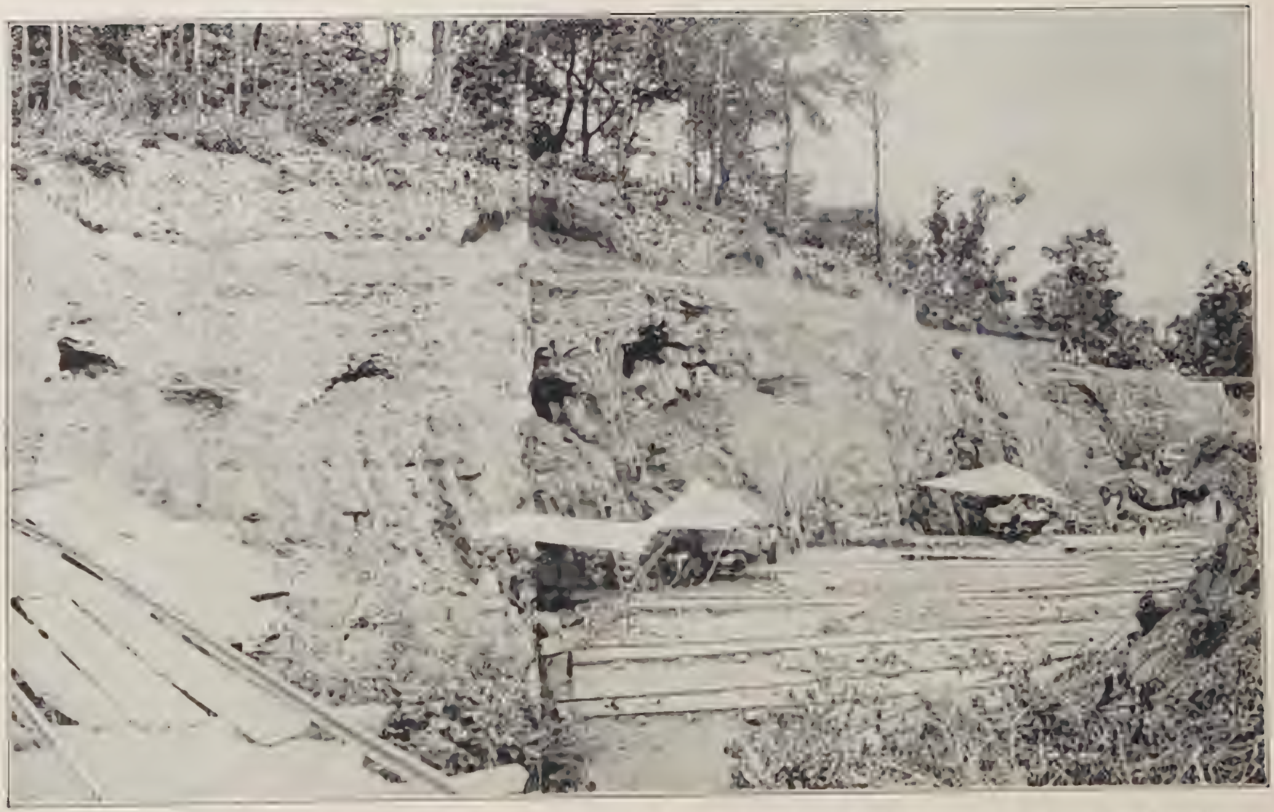

FIG. 155.—Bolivar flint-clay, Bolivar, Pa. This clay is about 22 feet thick and overlain by impure clay, coal, and sandstone. (After Hopkins.)

sylvania State College.[1] In this Affelder states that at Pittsburgh, where 320 feet of strata of the Conemaugh formation are exposed between the level of the Monongahela River and the outcrop of the Pittsburgh coal near the hilltop, almost all of the rock is shale, most of which is well adapted to the manufacture of brick. The color is variable, but most of the beds are red-burning. Fire-clays do not appear to be abundant in the Conemaugh, but some low-grade ones have been found and used to advantage for the manufacture of building- and paving-brick,

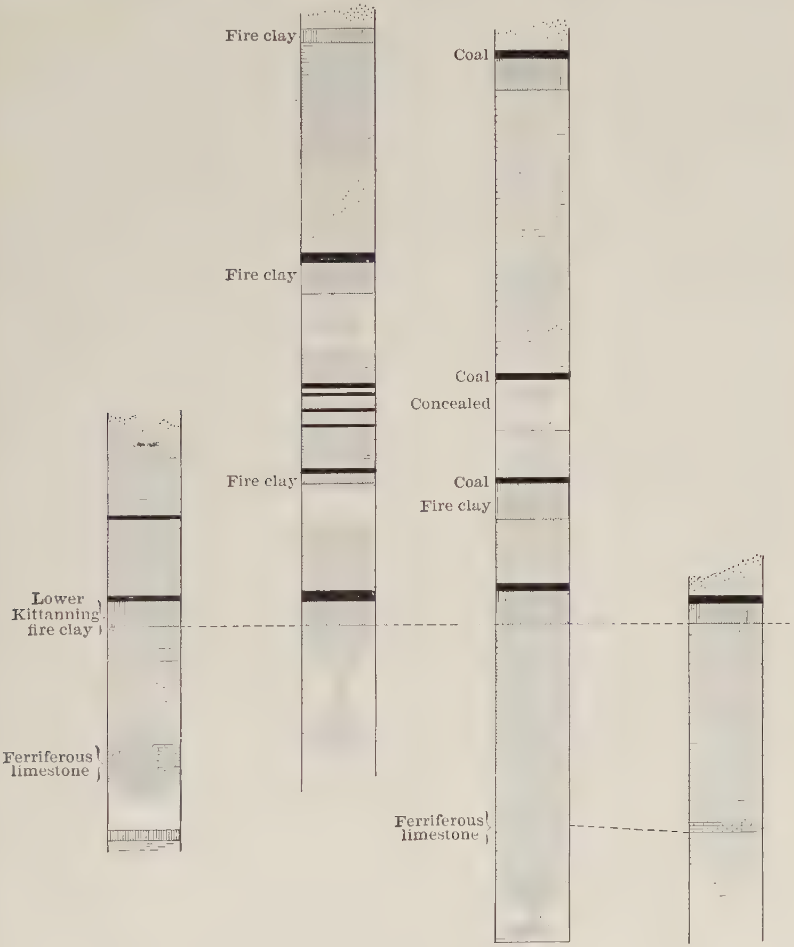

FIG. 156.—Vertical sections near New Brighton, Pa. (After Hopkins.)

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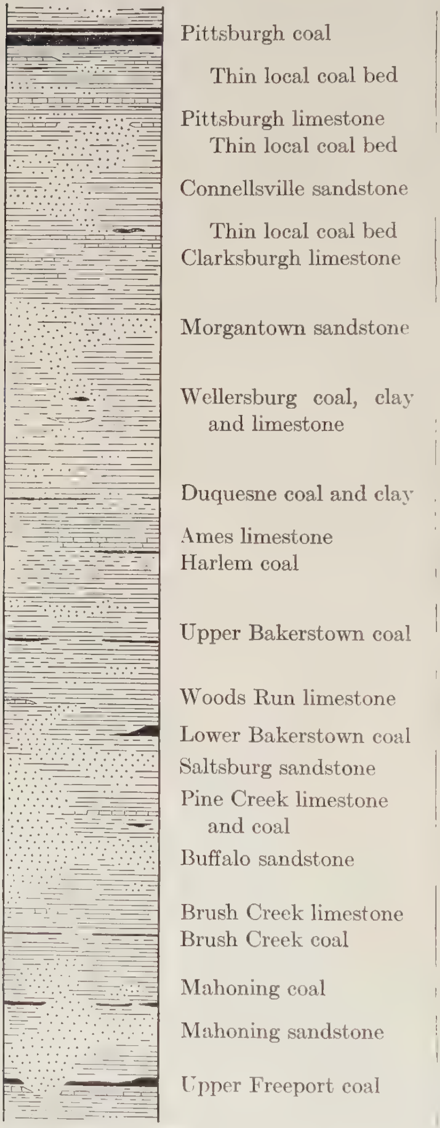
[1] The Clays of Western Pennsylvania, Ann. Rept., Pa. State College, 1897, p. 137.



Composed chiefly of shale. Sandstone beds are locally very thick and prominent. Contains several coal beds which locally are thick enough to mine, but only two of which are being mined today (1923). The upper half of the group includes two limestone beds which in the southern half of the quadrangle are frequently thick enough to make it profitable to quarry them. The lower half of the group contains three thin fossiliferous limestone beds which are important stratigraphic "markers." The red beds of this group are often conspicuous in the landscape.

FIG. 157.—Section of Conemaugh series in Pennsylvania. (After Johnson, Greensburg Atlas, Pa. Geol. Surv., 4th series, 1926.)

as at Harmonville. Of the fifty-seven yards listed in the report just referred to over two-thirds use shale wholly or in part.

Ashley notes an important shale bed in the Conemaugh, just above the Mahoning sandstone, which is especially well developed in northeastern Indiana County and southeastern Jefferson County (Ref. 2). In southwestern Cambria County a flint-clay is found close to the top of the Mahoning sandstone in the Johnstown district. It may grade into plastic clay (Ref. 15). Promising shales also occur in Armstrong and Indiana counties (Ref. 17).

Monongahela Series or Upper Coal-measures.—These show their greatest development in southwestern Pennsylvania, and while the shale-deposits do not appear from published reports to be as abundant as in West Virginia, still occasional thick beds of shale occur.

An important clay-parting, 6 to 10 inches thick, is found in the Pittsburg coal-bed, and is used in the Monongahela Valley. It has to be removed in mining the coal and can hence be made a source of profit. The shale over the coal has been used at Fayette City for making red brick, while at Pittsburg the shale of this group is used for making brick and terra-cotta lumber.

PLEISTOCENE CLAYS

These are distributed over most of the State. They are of superficial character and rarely of great extent. Around Philadelphia the Columbian loams have for many years been worked for both common and pressed brick.

In western Pennsylvania clays are found under many river terraces, notably along the Allegheny, Monongahela, Beaver, Ohio, and Youghiogheny.[1] Along the Ohio and Beaver rivers there are three well-marked terraces, lying respectively 30–50, 150, and 200–250 feet above the river-level. Clays, which are dug in the highest and lowest of these, are used for brick and earthenware, and excellent results are sometimes also obtained by mixing these with shales.

In other parts of the State many local deposits are employed for common and pressed brick.[2]

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[1] Hopkins, Ann. Rep. Pa. State College, 1897, p. 144.

[2] Many localities are noted in Prof. Pap. 11, U. S. Geol. Surv., pp. 235–238.

ANALYSES OF PENNSYLVANIA CLAYS

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Silica (SiO_2)	73.30	59.83	46.26	51.72	44.04	55.21	45.65	58.75
Alumina (Al_2O_3)	17.43	26.96	36.25	21.73	39.44	31.18	34.73	25.17
Ferric oxide (Fe_2O_3)	0.37	1.98	1.64	FeO 7.87	FeO 0.94	0.07	3.54	FeO 2.19
Lime (CaO)	0.02	0.11	0.19	0.06	0.07	0.18	0.11	0.71
Magnesia (MgO)	1.28	0.50	0.32	2.37	0.11	0.11	0.61	0.93
Potash (K_2O)	2.99	0.94	1.69	4.58	0.72	0.23	5.75	3.53
Soda (Na_2O)	0.17	0.24	0.85					
Water (H_2O)	4.68	9.56	13.54	......	......	13.02	......	8.11
Titanium oxide (TiO_2)	......	......	......	0.87	......	......	......	1.05
Ignition	......	......	......	10.78	14.13	......	9.65	
Sulphur trioxide (SO_3)	......	......	......	......	trace			
Organic and loss	......	......	......	......	......	0.23		
Mang. dioxide (MnO_2)	......	......	......	......	......	......	......	trace

	IX.	X.	XI.	XII.	XIII.	XIV.	XV.	XVI.
Silica (SiO_2)	50.37	62.89	51.92	55.33	46.16	67.78	61.81	54.09
Alumina (Al_2O_3)	32.89	21.49	31.64	27.84	26.97	16.29	27.18	19.95
Ferric oxide (Fe_2O_3)	FeO 1.64	FeO 1.81	FeO 1.13	FeO 2.91	7.21	4.57	6.96	9.84
Lime (CaO)	0.31	0.38	0.03	0.58	2.21	0.60	2.00	0.72
Magnesia (MgO)	0.35	0.56	0.44	0.75	1.52	0.72	1.50	1.55
Potash (K_2O) Soda (Na_2O)	0.29	2.52	0.40	3.91	3.24	2.00	......	3.31
Water (H_2O)	......	7.58	13.49	7.49	11.22	6.34	......	2.20
Titanium oxide (TiO_2)	1.03	1.82	1.16	1.14	0.74	0.78		
Ignition	13.76	......	......	CO_2 .45	....	......	......	8.98
Moisture	......	1.16						

I. Mount Holly, white mixed clay, residual.
II. Conshohocken, parti-colored clay, residual.
III. Brandywine Summit, residual.
IV. Wilmarth Station, Mercer fire-clay.
V. Fletcher mine, Elk County, Sharon fire-clay.
VI. Somerset County, Mt. Savage fire-clay.
VII. Sandyridge, Clearfield County, Brookville under-clay.
VIII. Kittanning, Clarion coal under-clay.
IX. Allegheny Furnace, ferriferous coal under-clay.
X. New Brighton, Kittanning lower coal under-clay.
XI. Salina, Kier Bros., Bolivar under-clay, flint-clay.
XII. Salina, Kier Bros., Bolivar under-clay, plastic clay.
XIII. New Brighton, Mendenhall & Chamberlain, terrace-clay.
XIV. New Brighton, Elverson & Sherwood, terrace-clay.
XV. Allegheny, Allegheny Brick Co., analysis of brick.
XVI. Butler, Butler Brick and Tile Co.
Numbers I–XVI from U. S. Geol. Surv., Prof. Pap. 11.

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27. Scattered notes in Reports of Sec. Pa. Geol. Surv., especially H4, H5, C4, C5.

RHODE ISLAND

This State has very limited clay resources. Glacial clays are known at a few points around Narragansett Bay, but the principal occurrence is found in the town of Barrington, where the deposits of bluish-gray, sometimes sandy clays are worked for the manufacture of common brick.

REFERENCE ON RHODE ISLAND CLAYS

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SOUTH CAROLINA

The northwestern part of the State is underlain by crystalline rocks which extend to the edge of the Coastal Plain. In this area there are a number of residual clays which can be used in common brick manufacture. Deposits of white residual clay (Ref. 1) from pegmatite have been prospected near Abbeville, but there is no commercial production.

The most important clay deposits in the State are the white clays of probable Upper Cretaceous age which form a belt across the State lying southeast of the Fall line (Fig. 158). These white sedimentary clays which are erroneously called kaolins, occur as lenses which are associated with whitish sands and are overlain by sands of a ferruginous character (Fig. 159).

They form the basis of an important clay-mining industry the product from the pits being used in whiteware, floor- and wall-tile, for pigments, in paper manufacture, etc.

Analyses and physical tests of some of these white clays are given below:

Analyses of South Carolina White Clays

	I	II	III	IV
SiO_2..........	44.23	45.69	79.40	53.19
Al_2O_3.........	38.98	37.47	10.70	33.41
Fe_2O_3.........	0.77	1.01	2.57	1.67
CaO..........	0.03	trace	0.58	0.10
MgO..........	0.07	0.08	1.05	0.25
K_2O..........	0.26	2.00	1.21	0.66
Na_2O.........	0.55	0.69	0.23	0.12
TiO_2..........	0.85	1.44	0.55	0.37
Ignition.......	13.85	13.98	3.94	10.63

I. Langley, S. Ca. III. Clarendon County, S. Ca.
II. Sievern, S. Ca. IV. Dents Pond.

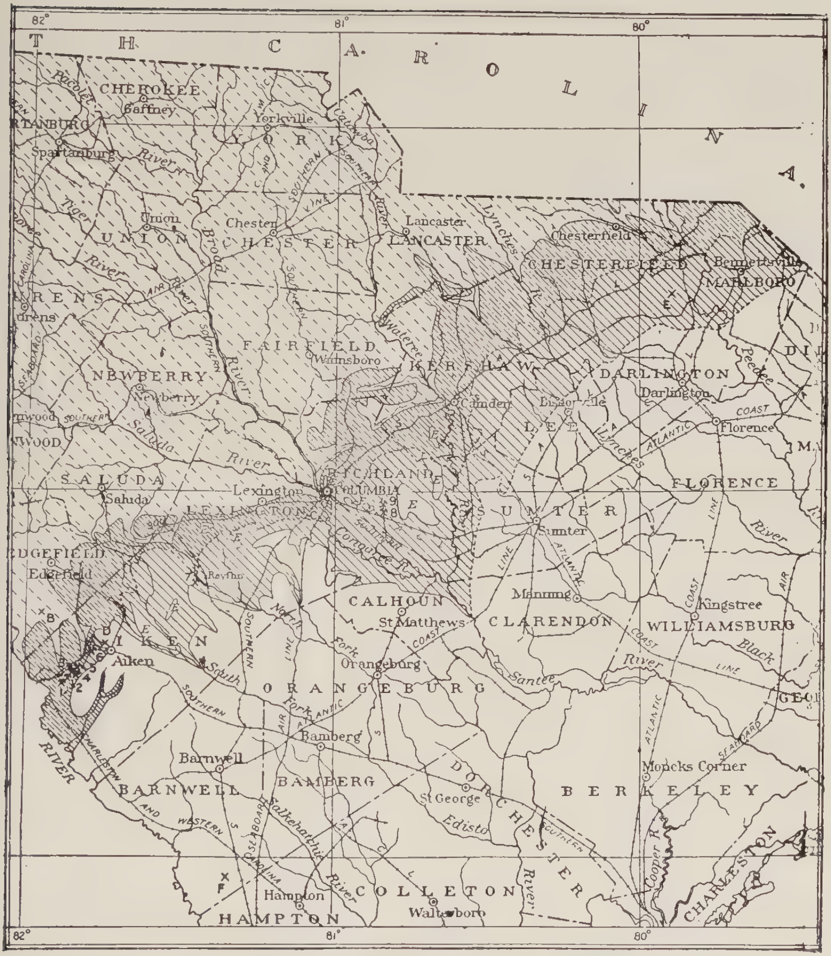

FIG. 158.—Map of white Cretaceous clay belt of South Carolina. (U. S. Geol. Surv., Bull. 708, 1922.)

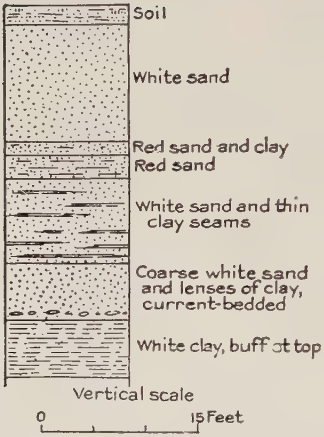

Fig. 159.—Section in pit of South Carolina Clay Co., south of Langley, S. Ca. (Bayley, U. S. Geol. Surv., Bull. 708, 1922.)

Physical Tests of South Carolina White Clays
(Made at U. S. Bureau of Mines)

	I	II	III
	Per cent	Per cent	Per cent
Water of plasticity	43.4	43.76	32.50
Volume air shrinkage	22.54	17.90	11.46
Linear air shrinkage	8.20	6.20	4.00
Fire shrinkage volume:			
1190° C	22.65	24.90	8.00
1250° C	25.30	25.80	12.20
1310° C	32.40	32.58	17.24
1370° C	41.70	40.24	30.50
1410° C	45.37	48.50	30.90
Fire shrinkage, linear, calculated:			
1190° C	8.20	9.1	2.70
1250° C	9.30	9.5	4.60
1310° C	12.20	12.30	6.10
1370° C	16.50	15.80	11.40
1410° C	18.30	17.30	11.60
Porosity:			
1190° C	40.97	37.64	30.90
1250° C	38.70	37.30	29.20
1310° C	31.20	32.83	26.58
1370° C	22.20	22.80	0.20
1410° C	9.81	6.20	0.00

I. White clay. Bath, S. Ca.
II. White clay near Warrensville, S. Ca.
III. White clay, Abbeville, S. Ca. Residual.

REFERENCES ON SOUTH CAROLINA CLAYS

1. Barker, M. E., Clay Resources of South Carolina, The Ceramist, VIII, p. 249 and 378, 1926.
2. Ries, H., Bayley, W. S., and others. High Grade Clays of the Eastern United States, U. S. Geol. Surv., Bull. 708, p. 79, 164, 211, 230, 1921.
3. Sloan, E., Clays of South Carolina, S. Ca. Geol. Surv., Ser. IV, Bull. 1, 1904.
4. Weigel, W. M., The White Clay Industry in the Vicinity of Langley, South Carolina, U. S. Bur. Mines, Month. Invest., No. 2832, 1922.

SOUTH DAKOTA

Very little information has been published regarding the clays and shales of this State, and it is difficult to discuss them by formations, as has been done with most of the other States.

Aside from scattered references, the best and most recent information is that given by J. E. Todd,[1] from which most of the facts below are taken.

Clays abound in many parts of the State, the most important deposits being found in the Cretaceous, which is largely composed of clay- or shale-deposits, but clays of the lower grades, are not wanting in the Pleistocene formations. None appear to have been noted from the Carboniferous. It seems likely that, owing to the absence of local demand, distance from important markets, and in some cases remoteness of the deposits from railroads, the development of the beds, unless of high grade, will be necessarily slow.

Kaolin, apparently derived from the weathering of a granite vein, has been reported from the vicinity of Custer, but much of it is said to be white-burning and of comparatively easy fusibility. The possibility of finding it in the Harvey Peak and Nigger Hill regions is also suggested.

Fire-clays are found at three or four horizons in the Fuson formation of the Cretaceous, and are best developed in the vicinity of Rapid City, where they have been used for fire-brick manufacture. Similar beds occur at Hot Springs. Analyses of the Rapid City clays are given below.

It is possible that fire-clays may underlie the lignite beds of the Laramie in the Cave Hills, but no search has been made for them.

Potter's clays have not been definitely located, but there are many drab and gray plastic shales in the Fuson, Dakota, Pierre, and Laramie formations of the Cretaceous, which might answer for this purpose. Some of the Tertiary beds may also prove of value.

These materials are distributed in all parts of the State, but east

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[1] S. Dak. Geol. Surv., Bull. 3, pp. 101–107, 1902.

FIG. 160.—Beds of Cretaceous fire-clay, southwest of Rapid City, S. Dak. (After Todd, S. Dak. Geol. Surv., Bull. 3, p. 113, 1902.)

FIG. 161.—General view of valley at Thurber, Tex., underlain by paving-brick shale. (Photo by H. Ries.)

of the Missouri River the heavy covering of glacial deposits renders them more or less inaccessible, except where they have been exposed along the larger streams.

Brick-clays have not been extensively worked. Professor Todd states that: "Over much of the State, particularly in close proximity to the principal towns, good brick-clay is not very accessible. This results from the fact that the settlements have been mainly made in the glacial region east of the Missouri and in the mountainous region of the Black Hills, where the clays are generally stony. . . . In the regions between, where clay is more abundant, the population has been small and fuel scarce."

Alluvium is used for common and pressed brick at Vermilion, Clay County, and the same products are made from similar materials at Rapid City, De Smet, Big Stone City, Lead City, etc.

The glacial clays are usually unsatisfactory, because of the pebbles and concretions which they contain.

ANALYSES OF SOUTH DAKOTA CLAYS

	I	II	III
Silica (SiO_2)	83.30	76.78	81.98
Alumina (Al_2O_3)	12.30	14.43	13.08
Ferric oxide (Fe_2O_3)	0.80	0.18	0.21
Lime (CaO)	1.30	2.18	1.46
Magnesia (MgO)	trace	0.95	0.31
Alkalies (Na_2O,K_2O)	....	trace	trace
Loss on ignition	....	4.62	4.07
	97.70	99.14	101.11

I. Rapid City.
II. East slope of ridge at Rapid City.
III. Rockerville Hill, Rapid City.
From S. Dak. Geol. Surv., Bull. 3.

REFERENCES ON SOUTH DAKOTA CLAYS

1. Todd, J. E., The Clay and Stone Resources of South Dakota, Eng. and Min. Jour., LXVI, p. 371, 1898.
2. Todd, J. E., The Mineral Resources of South Dakota, S. Dak. Geol. Surv., Bull. 3.

TENNESSEE

The geologic formations occurring in Tennessee include pre-Cambrian, Cambrian, Ordovician, Silurian, Devonian, Carboniferous, Tertiary, and Pleistocene, but all of these are not important as sources of supply for the ceramic industry.

The pre-Cambrian rocks occur in small areas along the eastern border, while west of them, and folded into many narrow belts, lie rocks of Cambro-Silurian age. The Carboniferous extends from the eastern edge of the Cumberland Plateau westward to beyond the Tennessee River. A large area of Silurian is found in the central part of the State, while another is found along the Tennessee River in the southern half of the State. This is followed by a broad belt of Tertiary, which in turn is separated from the Mississippi River by a band of Pleistocene.

Pre-Cambrian Clays

No kaolin-deposits have been described from the crystalline area of eastern Tennessee, although it is probable that some at least exist, as the author has seen samples of kaolin from this region. They will be of little commercial value, however, unless located fairly close to lines of transportation.

Paleozoic Residual Clays

The rocks of the Palæozoic formations yield residual clays from both limestones and shales. These are usually impure, although often tough and plastic, and are much used for brick- and tile-making.[1]

Some of the highly siliceous clays derived from the Knox dolomite are refractory,[2] and fire-brick are made from them near Cleveland. At Smithville a white clay, derived from the slate in the upper part of the Fort Payne division, is used for pottery.

Ordovician

Ordovician shales are used at Johnson City for making hollow brick and tile, and at Kingsport, for face brick, tile, and terra cotta.

Carboniferous

There is but little recent reliable information relating to Carboniferous clays or shales in Tennessee.

J. M. Safford, in his report on the Geology of Tennessee published in 1869, refers to the following occurrences of clay in the Carboniferous:

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[1] Many scattered references, but of very brief character, are to be found in the U. S. Geol. Surv., Geol. Atlas Folios, as follows: No. 21 (Pikeville); 16 (Knoxville); 59 (Bristol); 4 (Kingston); 8 (Sewanee); 2 (Ringgold); 53 (Standingstone); 40 Wartburg; 27 (Morristown); 22 (McMinnville).

[2] U. S. Geol. Surv., Geol. Atlas, Folio No. 2 (Ringgold).

Near the Cumberland Iron Works, in Stewart County, is a bed of fire-clay of Lower Carboniferous age;[1] another occurs 4 miles southwest of Cumberland City, in Stewart County; in the valley of Crow Creek, near Anderson station, the coal-measures at the margin of the tableland show a fire-clay 3 feet thick, 163 feet below the top of the cliff;[2] in Franklin County, near the Grundy County line, and 4 miles northwest of the track of Sewanee road at the old Logan bank, is a bed of clay 115 feet below the conglomerate;[3] near the lower end of the Battle Creek Valley, in Marion County, is a bed of fire-clay 2 feet thick; 5 miles southeast of Tracy City, and 1½ miles from Parmly Bank, a bed of clay underlies the main Sewanee coal;[4] another occurs at the north end of Lookout Mountain, below the upper conglomerate.[5] Many of the under-clays of the coal-seams, according to Safford, are of refractory character.[6] Fire-clays, mostly undeveloped, are said to be associated with the coals in the areas covered by the following Geologic Atlas Folios: Standingstone, No. 53; Wartburg, No. 40 (used for pottery).[7]

In the Kingston region the beds of clay which underlie the coals are no doubt refractory in many cases, but they are wholly undeveloped.[8]

The Mississippian shales are worked at Chattanooga for the manufacture of tapestry, face, and common brick, as well as hollow blocks, interlocking tile, drain-tile, and turpentine cups.

At Oliver Springs and Robbins respectively, large quantities of face brick and vitrified brick are produced from shales associated with the coal measures.

CRETACEOUS

The Ripley formation, consisting mostly of sand, extends from north to south across the western part of the State, in a somewhat narrow belt. There are local deposits of clay. At Hollow Rock some sagger and ball-clay are dug, and some is also obtained from two localities in Henry County.

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[1] Safford, Geology of Tennessee, p. 349.

[2] Ibid., p. 372.

[3] Ibid., p. 373.

[4] Ibid., p. 380.

[5] Ibid., p. 385.

[6] Ibid., p. 513.

[7] See also Geologic Atlas U. S. Folio 33, Briceville; Folio 21, Pikeville; Folio 4, Kingston.

[8] Idem, Folio 4, Kingston.

TERTIARY

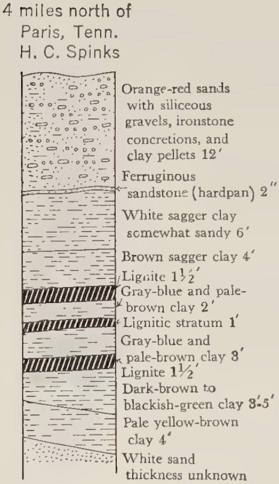
4 miles north of
Paris, Tenn.
H. C. Spinks
Orange-red sands with siliceous gravels, ironstone concretions, and clay pellets 12'
Ferruginous sandstone (hardpan) 2"
White sagger clay somewhat sandy 6'
Brown sagger clay 4'
Lignite 1½'
Gray-blue and pale-brown clay 2'
Lignitic stratum 1'
Gray-blue and pale-brown clay 3'
Lignite 1½'
Dark-brown to blackish-green clay 3-5'
Pale yellow-brown clay 4'
White sand thickness unknown

FIG. 162.—Section in Lagrange clays, 4 miles north of Paris, Tenn. (U. S. Geol. Surv., Bull. 708, 1922.)

The clays of the Lagrange formation in western Tennessee are the best in the State. The clay occurs as lenses, which often are some acres in extent, and may have lignite associated with them. Sand and gravel, sometimes of considerable thickness usually overlies the clay (Fig. 162). The principal deposits are in Henry and Carroll counties, although they have also been found to some extent further south. Several grades of clay are frequently found in the same lens (Fig. 165). These clays form the basis of an important clay-mining industry, the product being shipped to a number of States. The types dug include ball-clays, refractory bond clays, sagger and wad clays. They are used in the manufacture of table and toilet ware, sanitary ware, electrical porcelain, art pottery, glass pots, graphite crucibles, etc.

PHYSICAL TESTS OF LAGRANGE CLAYS. (PARMELEE)

		I	II	III
Water of plasticity, per cent		35.5	31.8	27.2
Modulus of rupture, pounds per square inch		240	101	69
Linear air shrinkage, per cent		8.82	5.2	5.6
Linear fire shrinkage, per cent,	Cone 2	6.0	11.2	....
	Cone 9	13.3	14.3	13.2
	Cone 13	13.0	11.9	....
Porosity, per cent	Cone 2	0.78	2.1	24.8
	Cone 9	1.8	1.6	8.8
	Cone 13	15.0	4.5	5.5
Cone of fusion		32	28	28

I. Ball clay near MacKenzie.
II. Stoneware clay near MacKenzie. III. Sagger clay, Henry.

ALLUVIAL CLAYS

Alluvial clays are found in many of the river valleys, and in most cases are the wash from the residual clays of surrounding areas. They often underlie the river terraces. These terrace-clays are used in the Maynardville area.[1] Others are common in the region around Morristown,[2] especially in the low grounds of the Lick Creek, Nolichucky, and French Broad valleys.

The following analyses of Tennessee clays have been gathered from different sources:

Analyses of Tennessee Clays

Locality.	SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	Alk.	H_2O.	Moisture.	MnO_2.	Remarks.
Loudon.	45.06	30.03	4.50	4.70	4.80	. . . . .	10	1	. . . . . .	Crossley, analyses of clays
Powdes Station.	68.35	12.96	6.44	0.23	1	2.14	7	8	0.9	J. W. Slocum, anal.
Chattanooga. . .	68.96	20.42	1.84	0.16	0.33	2.18	6.50	. . . . . .	trace	Tennessee Paving-brick Co.
Robbins.	70.57	15.19	7.97	0.78	0.32	2.80	. . . . .	. . . . . .	. . . . . .	Clay-worker, Dec., 1893

REFERENCES ON TENNESSEE CLAYS

1. Eckel, E. C., Stoneware and Brick-clays of Western Tennessee and Northwestern Mississippi, U. S. Geol. Surv., Bull. 213, p. 382, 1903.
2. Kirkpatrick, F. A., and Nelson, W. A., Tests on the Clays of Henry County, Tenn. Geol. Surv., Res. of Tenn., Vol. II, p. 406, 1912.
3. Nelson, W. A., Clay Deposits of West Tennessee, Tenn. Geol. Surv., Bull. 5, 1911.
4. Parmelee, C. W., Ball-clays of West Tennessee, Tenn. Geol. Surv., Res. Tenn., Vol. IX, p. 108, 1919.
5. Ries, H., Clays of the United States East of the Mississippi River, U. S. Geol. Surv., Prof. Pap. 11, 1903.
6. Ries, H., Bayley, W. S., and others, High Grade Clays of the Eastern United States, U. S. Geol. Surv., Bull. 708, 1921.
7. Schroeder, R. A., Ball Clays of West Tennessee, Tenn. Geol. Surv., Res. Tenn. Vol. IX, p. 81, 1919.

TEXAS

Deposits of clay or shale are scattered over all parts of Texas, but only those in the eastern part of the State have been systematically investigated. Indeed, it is not likely that those occurring in the western part will be developed to any extent for some time, owing to the sparsely settled character of the country and lack of transportation.

The annual reports of the First Geological Survey contain scattered references to clay-deposits, but few tests. In 1903 the University Mineral Survey undertook an examination of those deposits lying east of the 99th meridian, and the results of this work have appeared in bulletin form.[3] The following remarks, unless otherwise stated, deal with the area mentioned.

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[1] See Geologic Atlas U. S. Folio 75, Maynardville.

[2] Geologic Atlas U. S., Folio 27, Morristown.

[3] Univ. of Tex., Bull. 102, 1904.

The map, Fig. 163, shows the location of nearly all the deposits examined, their relation to the geology of the State, and the type of clay found

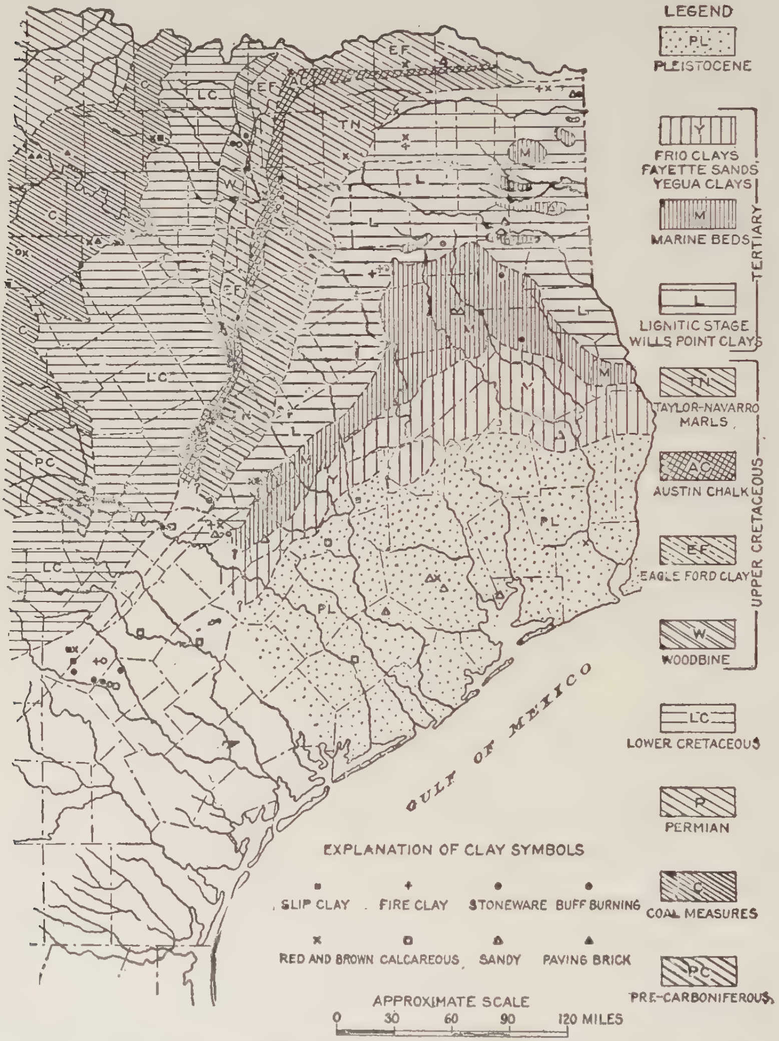

Fig. 163.—Map of eastern Texas, showing distribution of clay-bearing formations. (Compiled from various survey reports.)

at each locality. From this map it will be seen that the clay-deposits found within the area under discussion range from Carboniferous to Pleistocene in age, the older deposits being found in the northwestern part of the area, while those of the Cretaceous and Tertiary lie to the east, southeast, and south. The Pleistocene clays are found in part in a belt along the coast, and in part along many of the larger rivers, where they often underlie extensive terraces.

CARBONIFEROUS CLAYS

The Carboniferous rocks of northern Texas outcrop in a broad belt extending from the south side of the Colorado River Valley, between Lampasas and Concho counties, northward as far as the Red River in Montague County. This belt is about 250 miles long and averages about 45 miles in width. The rocks consist of a succession of shales and sandstones, together with occasional beds of limestone and coal, showing a gentle west and northwest dip of a few feet per mile. The entire series is subdivided into five groups (Ref. 2). Scattered through these are a number of beds of shale of excellent quality, some of which are associated with the coal-seams and could be mined in connection with them, while others outcrop on the surface (Fig. 161), where they are easily accessible for working.

These shales have been worked at only three localities, namely, Thurber, Millsap, and Weatherford, and are used for dry-pressed brick, stiff-mud paving-brick, and for pottery. Other good deposits are known to occur at Graham, Bridgeport, and Cisco. None of these, as far as known, are of refractory character. Some, as might be expected from their close association with coal-seams, are quite carbonaceous, and therefore of less value, because of the trouble they would cause in burning. The uniformity of the Carboniferous shale-beds is much greater than that of the Tertiary clays, and they moreover extend over greater areas.

CRETACEOUS CLAYS

Lower Cretaceous.—The formations of this age occupy an area to the east and south of the Carboniferous beds. They are not utilized, nor do they appear to contain any deposits of use for anything better than common brick. They can therefore be passed over. Near Leaky, Edwards County, Texas, there occur some most curious deposits of a white clay, which has usually been referred to as kaolin.[1] The material is a whitish clay, with pink and purplish mottlings, which forms vein-like deposits in the Edwards limestone. Scattered through it are crystalline masses of aragonite(?). Owing to the condition of the workings it is difficult to determine its exact relations to the surrounding limestone. As the deposits are of small extent and 40 miles from the railroad their commercial value is doubtful.

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[1] First Geol. Surv. of Texas, 2nd Ann. Rept., p. li, 1891.

Upper Cretaceous.—This division of the Cretaceous carries a number of important clay-deposits, some of which are of great extent, but unfortunately are not the most valuable clay-beds in the State.

The Upper Cretaceous rocks extend across Texas in a broad belt from the Red River north of Sherman down to Eagle Pass, which lies about the middle of the band. Fort Worth is on the western edge and Austin towards the southeastern border. A second belt extends along the Red River, with narrowing width, until it passes out of the State in the northeastern corner. Since the dip is to the southeast, the older beds are found along the western edge of the belt, and the higher or younger ones on the east where they pass below the Tertiary strata. Owing to the dissimilarity of the several numbers of this group, it becomes necessary to refer to them individually, beginning with the oldest.

Woodbine formation.—This consists of a series of sandstones, clays, and clayey sands, often containing leaf impressions and lignite. While the clay-beds are usually sandy or even bituminous, they become locally pure enough, as at Denton, to be utilized for clay-products, although even here the beds are rarely of great extent and usually interbedded with sands. The clays, which are worked at both Denton and Lloyd, closely resemble the stoneware-clays of the Tertiary beds to the southeast. They are mostly of very plastic, semi-refractory, buff-burning character and are utilized for both common stoneware and pressed brick.

Eagle Ford formation.—This includes a series of bituminous clay-shales, which in places contain thin limestone beds. It is one of the most extensive and thickest clay-bearing formations in the entire State of Texas, and occupies a rather long narrow belt, as shown in Fig. 163. While the Eagle Ford clay is of great thickness and well located for working, it contains about all the undesirable elements that a clay might have, namely, concretions, limestone pebbles, gypsum lumps, and even pyrite. Moreover, its bituminous character, as well as extreme toughness, causes great trouble in its manipulation, and practically forces the clay-worker to mold it by one method, the dry-press process, other means yielding a brick of too dense character to permit the carbon in the clay to burn off. The clay is red-burning, and extensively used for bricks around Paris, Sherman, Dallas, and Waco.

Taylor-Navarro marls, overlying the Eagle Ford stratigraphically but separated from it by the Austin Chalk, form an extensive belt of clay, which parallels that of the Eagle Ford formation. The beds are marly clays, and in their general physical and chemical properties bear a close resemblance to the Eagle Ford beds. The Taylor marls are not clearly distinguishable from the Navarro marls, which outcrop to the southeast of them and resemble them closely, and for this reason the two are included under a single head.

The Taylor-Navarro marls are all plastic, sometimes glauconitic, red-burning clays, and are worked for dry-press brick at Cooper, Greenville, Corsicana, Taylor, and Ferris.

At Eagle Pass, which lies outside the east and central Texas area studied, the Eagle Pass formation, which occurs at the top of the Upper Cretaceous, contains shales associated with the coals, and while some of these at least are probably adapted to the manufacture of clay-products, no tests of them are available.

Tertiary Clays

The clays found in the Tertiary formations include the most important ones in eastern Texas, but, owing to the lenticular character of the beds and the enveloping deposits of sand with which they are frequently associated, prospecting for them is often rendered more or less difficult. From the wide distribution of the deposits (Fig. 163) it would appear that in certain belts of the Territory at least, as mentioned below, clays are to be sought for with excellent chances of success.

In Webb County, west of Laredo in southern Texas, shales are found associated with the Eocene coals, and some of those obtained from the mines at Cannel are weathered and then shipped to Laredo for making dry-pressed brick.

The other Tertiary beds of eastern Texas consist largely of unconsolidated materials which range from coarse gravels to very fine clay, but containing occasional beds of sandstone, limestone, and lignite. Several members are recognized, namely, Will's Point, Lignitic, Marine, Yegua, Fayette, and Frio. Of these only the Lignitic and Marine are of importance.

Lignitic.—These beds outcrop in a long but irregular belt (Fig. 163), and contain the following types:

1. Beds of plastic, buff-burning, semi-refractory clay associated with the lignite deposits; they are well adapted to the manufacture of pressed brick.

2. Red-burning, plastic, gritty clays, overlying the lignites, and worked at Rockdale for dry-pressed brick.

3. Red-burning, tough, shaly clay, occurring at New Boston and Sulphur Springs.

4. A widely distributed series of grayish, highly plastic clays of

refractory or semi-refractory character, and used for stoneware, fire-brick, etc. The following analyses p. (431) represent groups I, II, III.

ANALYSES OF TERTIARY CLAY TYPES

	I	II	III
Silica (SiO_2)	69.33	72.99	70.65
Alumina (Al_2O_3)	19.38	14.70	18.14
Ferric oxide (Fe_2O_3)	1.06	4.5	0.82
Lime (CaO)	0.86	0.6	0.339
Magnesia (MgO)	0.86	0.3	0.628
Potash (K_2O)	trace	1.5	0.41
Soda (Na_2O)	0.08	0.7	0.55
Titanic acid (TiO_2)	1.40	1.00	1.14
Water (H_2O)	5.49	4.20	6.18

Stoneware is made from these clays at Elmendorff, Athens, etc.; fire-bricks at Athens and Sulphur Springs; sewer-pipe at Saspamco, and pressed brick at Elgin, Athens, Malakoff, etc.

Marine beds.—These are usually of sandy or glauconitic character, but here and there carry clay-deposits of some economic value, and adapted to making buff brick and stoneware. They are worked at Nacogdoches, Henderson, and Rusk.

PLEISTOCENE

This formation includes clays of several types. They form a rather broad belt along the Gulf Coast (Fig. 163), where they are mostly of sandy character, the Beaumont clays worked for brick around Beaumont and Houston being the most notable exception. These are tough, plastic, brown, blue, and yellow clays, carrying irregularly distributed nodules of limestone and underlying a broken belt extending from Calhoun County to Jefferson County. They are all red-burning, and used chiefly for common brick and to a lesser extent for dry-press brick.

A second important type includes the river silts found underlying the terraces along many of the large rivers, such as the Rio Grande, Colorado, Neches, etc. These clays are always silty or sandy and highly calcareous, the lime carbonate being present as concretions, lumps, shells, or in a finely divided condition, and forming at times over 50 per cent of the material without apparently diminishing its plasticity. They are especially well seen and extensively worked at Austin and Laredo. Though chiefly used for common brick, these clays have also been worked for pressed brick, and in a few localities, as near San Antonio, they are of the proper character for employment as a slip for stoneware. For practical purposes the clays found within the area just discussed can be divided into the following groups: I. Fire-clays; II. Stoneware-clays; III. Brick-clays; (*a*) Buff-burning, non-calcareous; (*b*) Red and brown-burning; (*c*) Calcareous; (*d*) Sandy; IV. Paving-brick clays;

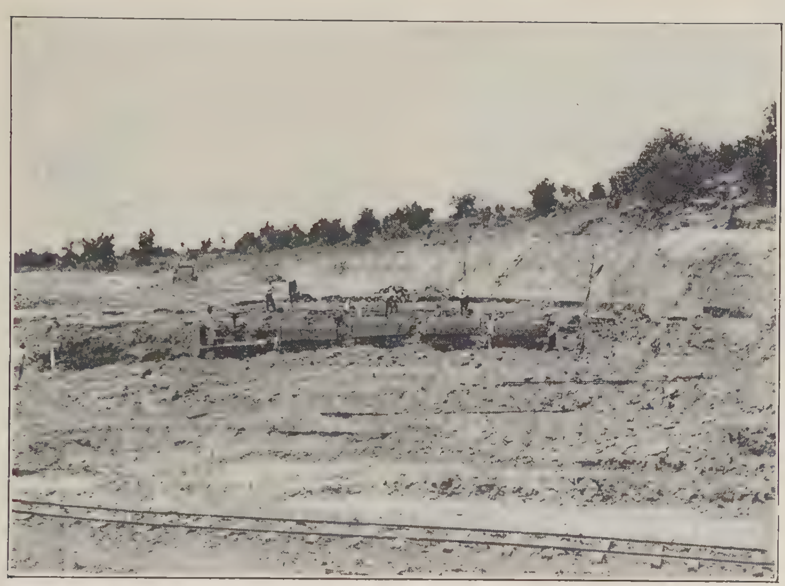

FIG. 164.—Bank of sewer-pipe clay in Lignitic (Tertiary) formation, Saspamco, Texas. Shows electric system of haulage. (Photo by H. Ries.)

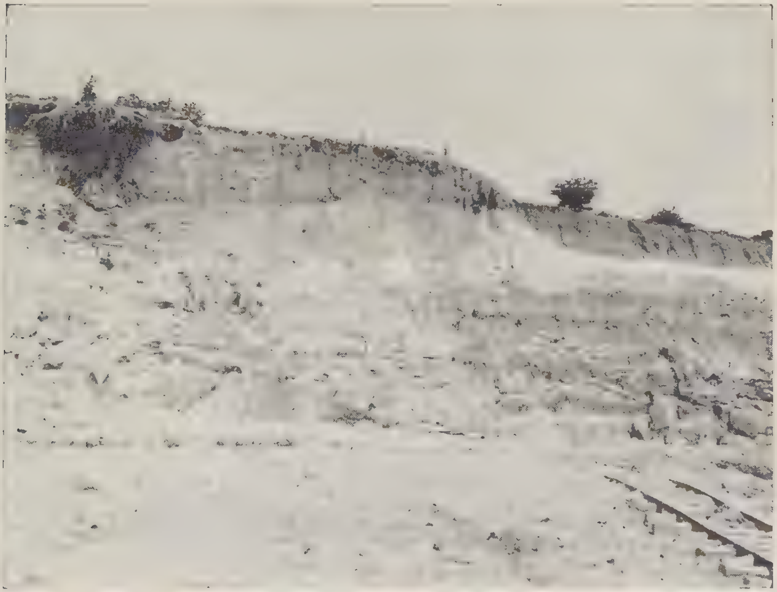

FIG. 165.—Clay pit in Lagrange clays near Whitlock, Tenn. The section shows several different grades. (H. Ries, photo.)

V. Slip-clays. Their distribution is shown on the map Fig. 163 and a few representative analyses are given below.

ANALYSES OF TEXAS CLAYS

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Silica (SiO_2)	63.07	63.43	45.44	55.10	49.45	73.00	72.9	64.84
Alumina (Al_2O_3)	19.43	23.42	40.30	23.80	17.11	15.79	14.7	22.44
Ferric oxide (Fe_2O_3)	4.75	1.15	0.54	3.51	3.45	0.63	4.5	0.80
Lime (CaO)	1.32	0.45	trace	3.28	12.67	1.29	0.6	trace
Magnesia (MgO)	0.50	1.23	trace	1.24	1.77	1.53	0.3	0.74
Potash (K_2O)	......	0.07	trace	0.50	0.13	0.10	1.5	0.12
Soda (Na_2O)	......	0.26	0.38	0.21	0.21	0.16	0.7	0.71
Titanic acid (TiO_2)	1.47	1.13	trace	1.05	0.70	0.43	1.0	1.40
Water (H_2O)	6.90	7.00	13.29	6.00	4.84	5.76	4.2	6.42
Sulphur trioxide (SO_3)	0.15	......	......	3.37	2.00			
Organic matter	......	0.40	......	......	......			
Carbon dioxide (CO_2)	......	......	......	1.75	7.10			
Total	97.59	98.54	99.95	99.81	99.43	98.69	100.5	97.47

	IX.	X.	XI.	XII.	XIII.	XIV.	XV.
Silica (SiO_2)	74.04	66.01	57.01	77.75	49.40	90.00	53.6
Alumina (Al_2O_3)	15.15	18.82	11.85	11.04	17.90	4.60	9.0
Ferric oxide (Fe_2O_3)	0.50	6.33	3.02	3.19	4.50	1.44	2.6
Lime (CaO)	0.50	0.55	9.56	0.84	9.50	0.10	17.8
Magnesia (MgO)	0.27	1.88	1.20	0.38	1.88	0.10	1.2
Potash (K_2O)	0.42	0.16	0.75	......	......	trace	1.8
Soda (Na_2O)	1.12	0.08	2.01	......	trace	trace	trace
Titanic acid (TiO_2)	1.31	0.95	1.13	1.23	1.05	0.70	.8
Water (H_2O)	6.00	4.80	4.00	3.24	4.58	3.04	1.
Sulphur trioxide (SO_3)	......	......	......	0.51			
Organic matter	......	......	......				
Carbon dioxide (CO_2)	......	......	8.00	......	9.55	......	11.6
Total	99.31	99.58	98.53	98.18	98.36	99.98	99.40

PHYSICAL TESTS OF TEXAS CLAYS

		I.	II.	III.	VI.	VIII.	IX.
Per cent water required		25.3	23.1	44	33	33	30.8
Plasticity		good	good	low	high	high	high
Average tensile strength, lbs. per sq.in.		333	202	159	487	304	257
Air-shrinkage, per cent		7.7	9.6	6.2	12.4	9.3	10.2
Cone 05	Fire-shrinkage, per cent	5.6	5	5	4*	1	1.6
	Absorption, per cent	3.58	2.02	32.79	......	12.9	11.44
Cone 1	Fire-shrinkage, per cent	6.3	......	10	4*	2.7	3.3
	Absorption, per cent	0.10	......	20.47	......	7.87	6.57
Cone 5	Fire-shrinkage, per cent	......	......	13.7	......	3.5	5.7
	Absorption, per cent	......	......	10.7	......	3.15	2.83
Cone 9	Fire-shrinkage, per cent	......	vit'd	14.7	......	......	9.4
	Absorption, per cent	......	......	8.6	......	......	0.82
Cone of fusion		5	14	35	5	12	28
Color after burning		red	buff	white	red	red	buff

* Dry Pressed.

Physical Tests of Texas Clays—*Continued*

		X.	XI.	XII.	XIII.	XIV.	XV.
Per cent water required		23.1	37.4	23.1	23	25.4	25.3
Plasticity		good	high	good	high	low	good
Average tensile strength, lbs. per sq. in.		155	154	303	316	77	253
Air-shrinkage, per cent		8.5	11.6	9.4	9.3	4	6.2
Cone 05	Fire-shrinkage, per cent	0	5.33*	0.3	0.4	−0.3	−4.7
	Absorption, per cent	15.68	16.49	10.52	6.63	9.14	......
Cone 1	Fire-shrinkage, per cent	1.6	11.33*	0.3	0.8	0	1
	Absorption, per cent	13.13	5.77	9.39	4.43	9.45	23.49
Cone 5	Fire-shrinkage, per cent	3	......	0.4	......	0.7	7
	Absorption, per cent	14.05	......	7.29	......	9.55	5.95
Cone 9	Fire-shrinkage, per cent	4.3	......	......	......	1.3	......
	Absorption, per cent	6.83	......	......	......	8.39	......
Cone of fusion		30	5	9	5	12	7
Color after burning		buff	red	red	red	red	cream

* Dry pressed.

Localities of Preceding Analyses

No.	Location.	Age.	Use.
I.	Thurber, Erath County	Coal-measures	Paving-brick
II.	Top clay over lower coal, Minera, Webb County	Cretaceous	Unworked
III.	Leaky, Edwards County	“	“
IV.	Dallas, Dallas County	Eagle-Ford-Cretaceous	Brick
V.	Ferris, Ellis County	Taylor marls	“
VI.	S. E. of Lena, Fayette County	Tertiary	Unworked
VII.	Vogel mine, Rockdale, Milan County	Lignitic-Tertiary	Brick
VIII.	Saspamco, Bexar County	“ “	Sewer-pipe
IX.	Athens, Henderson County	“ “	Fire-brick
X.	New Boston, Bowie County	Tertiary	Pressed brick
XI.	Alazan Creek, San Antonio, Bexar County	Pleistocene	Slip-clay
XII.	Beaumont, Jefferson County	“	Pressed brick
XIII.	Houston, Harris County	“	“
XIV.	Colmesneil, Tyler County	“	Common brick
XV.	Austin, Travis County	“ terrace-clay	Common brick

Nos. VII and XV, S. H. Worrell, analyst; the rest analyzed by O. H. Palm.

REFERENCES ON TEXAS CLAYS

1. Deussen, A., Notes on Some Clays from Texas, U. S. Geol. Surv., Bull. 470, p. 302, 1911.
2. Drake, N. F., and Thompson, R. A., The Colorado Coal Field of Texas, Tex. Geol. Surv., 4th Ann. Rept., p. 357, 1893.
3. Kruson, J. H., Refractory Clays of Texas, Jour. Amer. Ceram. Soc., Vol. I, p. 446, 1918.
4. Mayer, A., Notes on Texas Kaolin, Trans. Amer. Ceram. Soc., Vol. X, p. 91, 1908.
5. Ries, H., The Clays of Texas, Univ. of Tex., Bull. 102, 1908; also Trans. Amer. Inst. Min. Engrs., Vol. XXXVII, p. 520, 1907.

6. Taff, J. A., The Cretaceous Area North of the Colorado River, Tex. Geol. Surv., 4th Ann. Rept., p. 241, 1893.

See also scattered references in the first to fourth annual reports of Texas Geological Survey, especially under county descriptions.

UTAH

Deposits of lake clay are common in many of the valleys, but do not as a rule make good brick. The upper few feet are leached of their lime and give a red brick, while the lower clay is commonly calcareous and makes a yellow product.

Most of the high-grade clays are found in the hills and mountains, especially in the Oquirrh and Lake ranges surrounding the Cedar Valley desert. They are mostly of Carboniferous age. Some deform at cone 33 and 34, and one deposit is white-burning.

A good red-burning, vitrifying clay is located in Owen Canyon, Summit County, and makes an excellent sewer-pipe, while good brick shales are found in Emigration Canyon, 6 miles from Salt Lake City. Fire-brick, assayer's crucibles and face-brick are made at Salt Lake City.

REFERENCE ON UTAH CLAYS

1. Greaves-Walker, A. F., The Commercial Clays of Utah, Trans. Amer. Ceram. Soc., XIII, p. 277, 1911.

VIRGINIA

The State of Virginia can be divided into three provinces: the Coastal Plain, Piedmont, and Mountain, the latter including the Shenandoah Valley.

In the first of these sedimentary clays predominate, in the second residual ones, while in the third residual clays and shales are most prominent.

Residual Clays

Piedmont province.—The crystalline rocks, consisting of granite, gneiss and schist, extend across the State from north to south in a belt of increasing width, whose western boundary follows approximately a line drawn from Harper's Ferry southwestward, passing a few miles east of Front Royal. The eastern edge coincides approximately with the "Fall line." There are also several belts of Triassic shales, sandstones and conglomerate.

Residual clays, derived especially from the crystalline rocks, are widespread, and with the exception of those noted below are all ferruginous and red-burning. In most cases they make a fair quality of common brick, but occasionally the material may be sufficiently smooth to be used for other purposes, as at Pamplin, Appomattox County, where it has been employed for making smoking pipes.

Kaolin derived from the weathering of pegmatite occurs at a few localities, especially in Pittsylvania County, but the deposits are not as a rule large, and yield a relatively small amount of washed product. A deposit near Roseland, Nelson County, formed from syenite pegmatite was formerly worked, and so was a second one in Henry County.

Mountain province.—Residual clays derived from both limestones and shales, especially the former, are widely distributed in the Shenandoah Valley, but they are little used. With the few exceptions noted below they are all red-burning. Both common brick and drain-tile can be made from them.

Along the western base of the Blue Ridge there occur some isolated pockets of white residual clay, which are associated with the brown iron ores. One of these has been worked near Buena Vista, Rockbridge County, for fire-brick manufacture.

Another, and relatively large one, derived from Cambrian shale, underlies the slope of the Blue Ridge southeast of Cold Spring, Augusta County. This material does not fire white, but is sufficiently so in its raw condition to be used as a filler for paper, etc.

Paleozoic Shales

No Paleozoic shales of value are found in the Coastal Plain or Piedmont provinces. In the mountain province shales ranging from Cambrian to Carboniferous in age occur in considerable abundance, but few of them will grind up to a plastic mass, when fresh. A slight amount of weathering in some cases renders them useful.

Among those which may be mentioned are: Slightly weathered Cambrian shale, used for bricks at New Glasgow; Devonian shales employed for bricks and hollow blocks at Rose Hill, Lee County, and Richlands, Tazewell County; and slightly weathered calcareous shales made into bricks at Tip Top, Tazewell County. Unworked deposits of promising character are found at Weldon, Pulaski County; North Mountain, Augusta County; Moccasin Gap, Scott County, etc.

Triassic

The formations of this age are found only in the Piedmont province, and in their unweathered condition rarely appear to be of value, except those found near Wolf's Trap.

Tertiary

The Tertiary beds with one exception occur in the Coastal Plain area. They consist of a series of clays, sands, marls, sandstones, greensands, and diatomaceous earth which dip gently southeast.

The clay deposits, which are mostly of Miocene age and usually of lenticular character, are most abundant towards the northwestern border of the Coastal Plain, and have been noted near Richmond, Bermuda Hundred, Curles Neck, etc. They are red-burning.

Some promising Eocene clays are known between Fredericksburg and Stafford Court House.

The diatomaceous earth forms an extended series of deposits along the Rappahannock River and around Richmond, but has been worked at only one locality, namely Wilmont, where it is used for making a porous brick.

What is apparently a Tertiary flood-plain deposit is found on the high ground near Radford. It is buff-burning, but is not worked.

Physical Tests of Virginia Clays and Shales

		I	II	III	IV	V	VI
Water plasticity, per cent		17	25	22	31	33	37
Linear air shrinkage, per cent		3	4.8	3.8	4	5.4	6.4
Tensile strength, pounds per square inch		36	80	40	40	60	71
Cone 010	Linear fire shrinkage, per cent	0	0	0	0	0	2.3
	Absorption, per cent	13.6	15.7	......	25.7	23.7	27.0
Cone 05	Linear fire shrinkage, per cent	2.6	1.6	1.0	3.3	0.7	3.0
	Absorption, per cent	9.6	10.7	13.4	18.4	21.9	23.5
Cone 03	Linear fire shrinkage, per cent	4.0	......	......	......	2.7	6.0
	Absorption, per cent	6.3	......	......	......	19.3	18.1
Cone 1	Linear fire shrinkage, per cent	4.5	5.0	2.6	9.0	3.0	4.4
	Absorption, per cent	4.6	0.4	9.1	3.7	18.4	17.7
Cone 3	Linear fire shrinkage, per cent	Vis-	5.0	3.6	3.6	......	.....
	Absorption, per cent	cous	0.0	4.5	1.1	......	.....
Cone 5	Linear fire shrinkage, per cent	......	4.3	4.3	......	......	.....
	Absorption, per cent	......	2.0	3.1	......	......	.....
Color fired		red	red	red	red	red	red

I. Mississippian shale, Weldon, Pulaski County.
II. Devonian shale, Richlands, Tazewell County.
III. Devonian shale, Moccasin Gap, Scott County.
IV. Slightly weathered shale, Tip Top, Tazewell County.
V. Residual clay from granite, Crozet.
VI. Residual clay from schist, Warrenton.

Analyses and Physical Tests of Virginia Clays

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.
Silica (SiO_2)	71.50	69.74	61.83	73.84	65.97	64.39	51.12	82.85	45.70
Alumina (Al_2O_3)	13.86	12.64	21.26	15.08	17.38	20.49	26.14	6.76	39.18
Ferric oxide (Fe_2O_3)	4.78	6.00 *	6.85	3.39	6.74	4.40	10.70	2.34	0.78
Lime (CaO)	0.56	1.46	0.38	0.62	1.16	0.17	0.10	0.35	0.44
Magnesia (MgO)	0.11	1.18	0.78	0.12	0.17	0.91	0.25	1.06	0.05
Potash (K_2O)	2.29	2.54	2.44	2.17	2.46	2.31	1.78	1.07	1.78
Soda (Na_2O)	0.81	0.92	1.01	0.71	0.93	0.54	0.77	0.99	0.20
Titanic acid (TiO_2)	1.44	0.06	0.08	1.22	1.04	0.08	0.47	1.09	0.28
Water (H_2O)	4.61	4.41	5.32	2.81	4.10	6.66	8.63	3.40	12.09 †
Total	99.96	98.95	99.95	99.96	99.95	99.95	99.96	99.91	100.50
Per cent water required	20.9	25.3	29.7	20.3	20.9	31.9	36.3	62.4	
Plasticity	good	low	good	good	good	high	fair	low	
Air-shrinkage, per cent	6.4	9.3	8.6	7.6	7.4	11.6	9.3	3.6	
Average tensile strength, lbs. per sq. in.	89.6	177.3	148.8	111.5	134.8	143.8	115.3	34.4	
Cone 010 Fire-shrinkage, per cent	0	0	0.3	0	0	1.3	0.6	1.3	
Cone 010 Absorption, per cent	17.40	18.2	22.04	16.3	17.7	16.9	28.2	50.96	
Cone 05 Fire-shrinkage, per cent	1.6	1.3	5.7	1.6	4.7	4	2.6	1.6	
Cone 05 Absorption, per cent	15.08	14.2	12.9	15.04	10.1	8.87	23.1	48.4	
Cone 1 Fire-shrinkage, per cent	5	2.3	10.7	3.6	8.3	7	7	4.6	
Cone 1 Absorption, per cent	7.1	7.54	0.12	7.2	1.5	1.5	12.06	41.4	
Cone 5 Fire-shrinkage, per cent	6.6	viscous	4.6	6.6	3	beyond	10.3	5.3	
Cone 5 Absorption, per cent	1.4	at cone 3	2.11	1.08	2.6	vit'n	3.5	38.3	
Color when burned	red	red	red	red	red	red	red	buff	white

* Also one per cent FeO.

† Includes 1.98 moisture.

I. Brick-clay, Richmond, Pleistocene.
II. Gray clay, 2 miles south of Chester, Tertiary, not worked.
III. Tile-clay, one mile northwest of Bermuda Hundred, Pleistocene.
IV. Brick-clay, Oldfield on James River. Pleistocene.
V. Tile-clay, 6 miles southeast of Richmond, Miocene, not worked.
VI. Blue clay for bricks, Suffolk, Pleistocene.
VII. Brick-clay between Stafford Court House and Fredericksburg, Eocene, not worked.
VIII. Diatomaceous earth, Wilmont on Rappahannock River, Miocene.
IX. Washed kaolin, Oak Level, Henry County. Unpublished analysis of Va. Geol. Sur.

Nos. I–VIII from Bull. II, Va. Geol. Surv., 1906.

PLEISTOCENE

Pleistocene clays occur at a number of points, but the deposits are with few exceptions of relatively shallow character and red-burning. They have been worked around Richmond for common brick and tile, as well as at Norfolk, Suffolk, Petersburg, and several points along the James River.

Around Alexandria the loams have been worked on a large scale for common and pressed brick, which supply the Washington market.

RECENT

Flood plain clays occur along some of the rivers and are occasionally worked for brick and tile.

REFERENCES ON VIRGINIA CLAYS

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2. Ries, H., Bayley, W. S., and others, High-grade Clays of the Eastern United States, U. S. Geol. Surv., Bull. 708, p. 18 and 99–104, 1921.
3. Ries, H., and Somers, R. E., The Clays of the Piedmont Province, Va., Va. Geol. Surv., Bull. 13, 1917.
4. Ries, H., and Somers, R. E., The Clays and Shales of Virginia West of the Blue Ridge, Va. Geol. Surv., Bull. 20, 1920.

WASHINGTON [1]

Clay-bearing formations.—The clay-bearing formation of Washington include: 1. Tertiary; 2. Pleistocene, (*a*) Glacial lake clays, and (*b*) others, mostly alluvial; 3. Residual clays from: (*a*) basalt, and (*b*) granite and pegmatites.

The important deposits of Tertiary shales and Glacial clays are in the western part of the State, especially around Puget Sound. In the eastern part of the State besides the residual clays there are only small deposits of alluvial and lake clays.

RESIDUAL CLAYS

Residual clays from basalt are found in the basalt region of southeastern Washington. They are high in iron, red-burning, and of rather uniform quality. Common brick, and in some cases, drain-tile have been made from them.

[1] Prof. Hewitt Wilson has supplied much of the material on Washington.

In the " Inland Empire " region of eastern Washington and extending over into Idaho are important deposits of white residual clay formed by the weathering of granite. This type of material has been worked at Freeman, and mixed with a more plastic clay and made into fire-brick at Clayton. Tests have indicated that the material when washed is also suitable for the manufacture of whiteware.

TERTIARY

There are important shale deposits of Eocene age in the southwestern part of the State and also some beds of fire-clay.

The Puget and Roslyn coal-bearing series contain shales that are well known and widely used. At Renton near Seattle light-gray shales of the Puget formation are being worked for face brick, common brick, and vitrified paving-brick. The same shale is also employed in sewer-pipe and architectural terra-cotta. Its thickness is not less than 150 feet.

At Kummer, 30 miles southeast of Seattle, there is a bed of highly carbonaceous flint fire-clay, which is interbedded with steeply dipping sandstone, shale and coal of the Kummer series. Its average cone of fusion is 32. The lightly calcined Kummer flint-clay is being used as 70 per cent of the Renton fire-brick mixture with 30 per cent of the Sumas plastic clay as a binder. With fine grinding in the wet pan the Kummer clay develops fairly good plasticity and tensile strength but without such treatment it is non-plastic.

The Sumas fire-clay which occurs interbedded with sandstone and conglomerate near Sumas, is not highly plastic, but sufficient strength is developed by grinding so that it can be used as a binder for the Kummer flint-clay.

PLEISTOCENE

Glacial lake clays of irregular occurrence are found associated with gravel and till. They are widely distributed throughout the western part of the State in the Puget Sound region, and there has been an extensive development of them in the western part of King County. The unweathered clay is blue and stratified, while near the surface the clay is weathered yellow and shows no stratification. These clays are used for common brick, hollow block, fireproofing, and drain-tile, but are not adapted to the making of vitrified products.

Alluvial, lacustrine, and estuarine deposits occur in the southwestern part of the State. They vary considerably in their properties, and are either red- or buff-burning. A few plants have used them for a good grade of structural products.

Silts and silty clays occur as terrace deposits in narrow valleys in the northeastern part of the State, and may be too silty to have much plasticity. A brown clay from Stevens County has been used as a slip for glazing stoneware.

Along the Columbia River in central and southern Washington there is found an alluvial silty clay often containing volcanic ash. It is red- to brown-burning, and is used for common brick.

USES OF WASHINGTON CLAYS

The alluvial clays in the northeastern part of the State, near Clayton, are used for paving-brick, sidewalk brick, and terra-cotta. North of Clayton stratified clay is worked for pottery. The glacial clays near Seattle are used extensively for common building-brick, hollow brick, sewer-pipe, and drain-tile. Alluvial clays along the Baker River in Skagit County are employed for Portland cement. The Tertiary shales near Seattle, and at some other localities are utilized for paving-brick, building-brick, terra-cotta, sewer-pipe, etc. The Kummer and Sumas clays, and the white residual clays are made into fire-brick.

The following tables give the analyses and physical tests of several Washington clays:

PHYSICAL TESTS OF TYPICAL CLAYS OF WASHINGTON

	I	II	III	IV	V	VI	VII
Water plasticity, per cent, dry basis	31.3	31.6	21.2	39.4	24.1	21.8	20.2
Linear dry shrinkage, per cent, dry basis	8.6	8.3	5.6	11.8	6.4	5.1	5.3
Dry transverse strength, pounds per square inch	433	240	255	799	560	704	664
General fired color	White	Buff	Buff-Brown	Buff	Buff	Red	Red
Cone deformation	34	32	28	30–31	23–26	6–7	5

Fired Properties, per cent.

	I		II		III		IV		V		VI		VII	
	S	A	S	A	S	A	S	A	S	A	S	A	S	A
Cone 08....	2.3	24.1	....	....	0.4	16.7	0.2	21.3	....	....	0.0	16.0	0.0	16.2
Cone 04....	6.8	12.0	....	....	0.6	16.6	2.3	16.5	1.7	19.6	2.1	14.5	3.3	10.0
Cone 1....	8.7	10.2	....	....	1.1	15.1	6.4	10.2	1.9	17.2	8.3	2.0	8.7	0.0
Cone 5....	8.7	9.8	5.0	24.1	2.0	14.7	11.3	8.0	2.2	15.7	....	....	7.0	0.0
Cone 9....	9.0	8.7	7.1	16.2	2.0	14.7	13.3	3.3	4.8	10.3				
Cone 15....	10.1	6.0	8.8	14.6	3.5	6.5	16.7	3.2	6.0	8.9				

S. Stands for linear fired shrinkage based on the dry length.

A. Is the per cent absorption at the different cones.

I. Kaolin fire-clay from the American Fire Brick Company, Mica, Wn. This sample is the washed or purified material from which the sand and mica have been removed. Possibilities for whiteware and paper. Without washing it is now used for refractories.

II. Kummer flint fire-clay from the Denny Renton Clay and Coal Company's Kummer mine. This sample has been wet-panned to increase the plasticity. Used for refractory purposes.

III. Fire clay from the Denny Renton Clay and Coal Company's Sumas mine. Used for general work.

IV. Clayton plastic fire-clay from the Clayton plant of the Washington Brick Lime and Sewer Pipe Company. It is used as a bond in fire brick, or is suitable for terra cotta, stoneware and other buff burning purposes.

V. Terra cotta body of the Gladding McBean and Company, Auburn, Wn. The clays were were mined at Green River.

VI. Paving Brick Shale from the Renton plant of the Denny Renton Clay and Coal Company.

VII. Glacial clay from the Builder's Brick Company, Seattle. This material is used for common, and face brick and hollow tile.

All the above tests and analyses from Bull. 18, Eng. Exp. Sta. University of Washington, Seattle.

Analyses of Washington Clays

	I	II	III	IV	V
SiO_2......	62.56	65.66	40.37	62.11	46.13
Al_2O_3.....	23.96	21.98	38.57	17.59	37.36
Fe_2O_3....	4.70	1.92	3.43	4.77	2.20
CaO......	....	....	0.67	1.53	0.65
MgO.....	Tr.	0.90	0.45	2.26	0.64
Na_2O.....	1.12	0.80	0.08	1.65	
K_2O.....			0.22	2.30	
TiO_2.....	....	....	....	0.51	
Moisture..	0.92	1.68	1.56	1.63	1.34
Ignition..	6.84	6.66	15.30	5.60	12.20
Total...	100.10	99.60	100.65	99.95	100.52

I. Light yellow lake clay, Stevens Co. Repressed brick.

II. Yellow clay, 6 miles north of Clayton, used for pottery.

III. Tertiary flint fire-clay, Kummer, King Co.

IV. Tertiary paving brick shale, Renton, King Co.

V. Stoneware clay, Palouse, Whitman Co.

REFERENCES ON WASHINGTON CLAYS

1. Landes, H., Clay Deposits of Washington, U. S. Geol. Surv., Bull. 260, p. 550, 1905.
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3. Shedd, S., Clays and Clay Industry of Washington, State College of Washington, 1910.
4. Wilson, H., The Clays and Shales of Washington Their Technology and Uses, Bull. Univ. Wash., Eng. Dept., Exper. Sta., No. 18.
5. Wilson, H., New Kaolin Deposits in the State of Washington, Clayworker, Vol. 78, p. 122, 1922.

WEST VIRGINIA [1]

With the exceptions of a few Pleistocene deposits, the clay-bearing formations of West Virginia are all of Paleozoic age.

Silurian

The residual clays derived from the Shenandoah limestone are found over large areas in Berkeley, Jefferson, and parts of Hardy, Hampshire, and Pendleton counties; they have been worked at Charlestown and Shepherdstown for red brick.

The shales of this age, known as the Martinsburg shale from their type occurrence at the town of that name, are hard and slaty when fresh, but weather down to a clayey mass which can be used for red-brick manufacture.

Red shales of Medina age and brown and gray Clinton shales outcrop in belts along the mountain-slopes of Mineral, Grant, Hardy, and Pendleton counties, but are not favorably located for working.

Devonian

The Devonian formations, according to Grimsley, consist of sandstones and shales, being found in Mineral, Grant, Hardy, Pendleton, Preston, Tucker, Randolph, Pocahontas, Greenbrier, and Monroe counties. They are grouped under the Hamilton, Chemung, and Catskill formations. Many of them are adapted to brick manufacture, but they are worked only at Elkins, Randolph County.

Lower Carboniferous

The Mauch Chunk shales, consisting of red and grayish-blue shales, green sandstones, and a few thin limestones, form a belt extending across the State from Preston County, through Tucker, Randolph, Pocahontas, Greenbrier, Monroe, and Summers counties.

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[1] Grimsley, G. P., W. Va. Geol. Surv., III, 1906.

The red shales and their residual clays form an excellent material for making red-pressed brick, the deposits moreover being well located, but up to the present time they have not been utilized.

CARBONIFEROUS

Pottsville series.—This contains clays, shales, sandstones, conglomerates, and coal-beds, but the only clay thus far worked is that occurring beneath the Homewood sandstone and known as the Mount Savage fire-clay. This is mined at Piedmont for fire-brick manufacture, and consists of both plastic and flint fire-clay, the two forming a bed about 15 feet thick.

Allegheny series.—In this series there are found a number of important coal-seams with their underlying fire-clays, the two important groups being the Kittanning coals and clays, and the Freeport group of coals and clays.

The two most valuable beds of fire-clay are the Lower Kittanning and the Bolivar.

The shales in the series have also been successfully used for building-brick.

Clarion clay.—The Clarion coal at the base of the Allegheny series is often underlain by a thick bed of fire-clay, but it is not worked in West Virginia.

Kittanning Clays.—The Lower Kittanning coal is very persistent through Ohio and Pennsylvania, but in West Virginia it is absent entirely as a workable bed in many regions of the State, and its place taken by the fire-clay.

The Lower Kittanning clay under the coal of that name is 5 to 15 feet at Hammond where it is worked.

Between the Upper and Lower Kittanning coals is an interval of sandstone, which at New Cumberland and Hammond carries the Middle Kittanning coal and its underlying fire-clay.

At New Cumberland, which is the largest brick-manufacturing center in the State, the Lower and Middle Kittanning clays are employed for the manufacture of building-brick and paving-blocks, and the Lower Kittanning clays for sewer-pipe. The shales between these two were formerly burned into common brick.

The following section at the Globe Works, given by Grimsley, is stated by him to be fairly typical of this region:

	Feet.	Inches.
Sandstone	40	
Coal	2	6
Flint-clay	6	
Gray shale-clay	4	
Blue shale-clay	12	
Sandstone floor	4	
Fine laminated shales	40	
Coal (Lower Kittanning)		3
Clay (Lower Kittanning)		10

The bottom clay is used for sewer-pipe, while the flint-clay and blue and gray shales are mixed together for brick and paving-blocks.

Upper Freeport clay.—There are some good outcrops of this clay on Decker's Creek above Morgantown near Dellslow, with good railroad connection, and could be easily developed.

Conemaugh series.—This series consists chiefly of sandstones and limestones, but contains scattered shale-deposits and some fire-clay. Overlying the Upper Freeport coal, or at times separated from it by the dark fossiliferous Uffington shales, are the Lower and Upper Mahoning sandstones. They are seen from Upshur southwest into Mingo, western Wyoming, and Raleigh counties. Between the two there is often found the Mahoning coal, which is worked near New Cumberland, while under the coal, and sometimes replacing it, there is a good bed of fire-clay found in a few regions and mined at Thornton, where it shows 18 feet of flint and soft clay. Near Ceredo, Wayne County, the clay is present without the coal.

At many points a shale-bed occurs between the two sandstones. Those worked around Charlestown may belong in part to this horizon, although some of the beds have been doubtfully referred to the Kanawha series of Virginia.

Overlying the Mahoning sandstone is the Cambridge limestone followed by the Ames limestone, and between these two is a mass of Pittsburg red shales, 30 to 100 feet thick, which extend from the Pennsylvania line southward to the Big Sandy River. These shales, which will undoubtedly prove of economic value, have been used at Huntington for roofing-tile manufacture. They also occur at Barlow, Charlestown, etc.

In Preston County near Reedsville, Masontown, and Kingwood, as well as near Collier and Wellsburg in Brooke County, the shales are partly replaced by the Saltzburg sandstone. Overlying the Ames limestone is the Birmingham shale.

A very complete section of the Conemaugh series is exposed at Morgantown, Monongalia County, but the only shales worked are the Pittsburg ones. They make a building- and paving-brick.

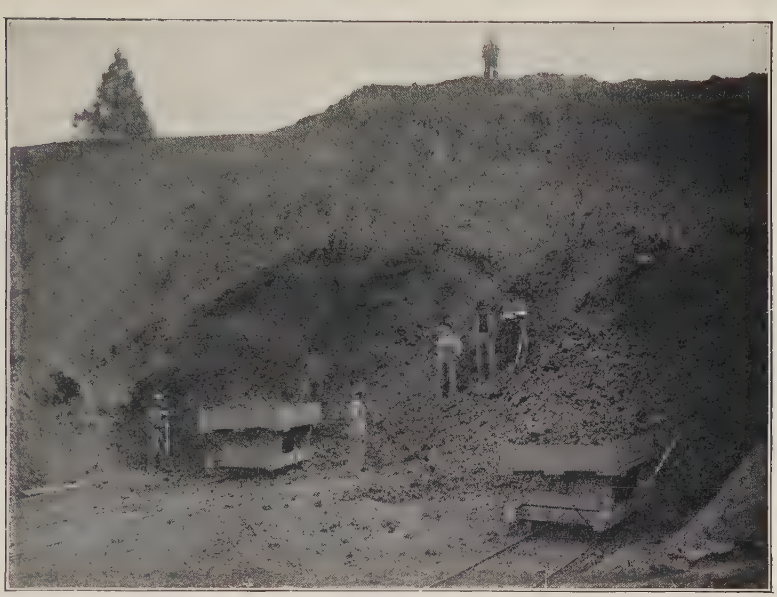

FIG. 166.—Red-burning brick-clay bank at Freeman, Wash. (Photo loaned by Washington Brick, Lime, and M'f'g Co.)

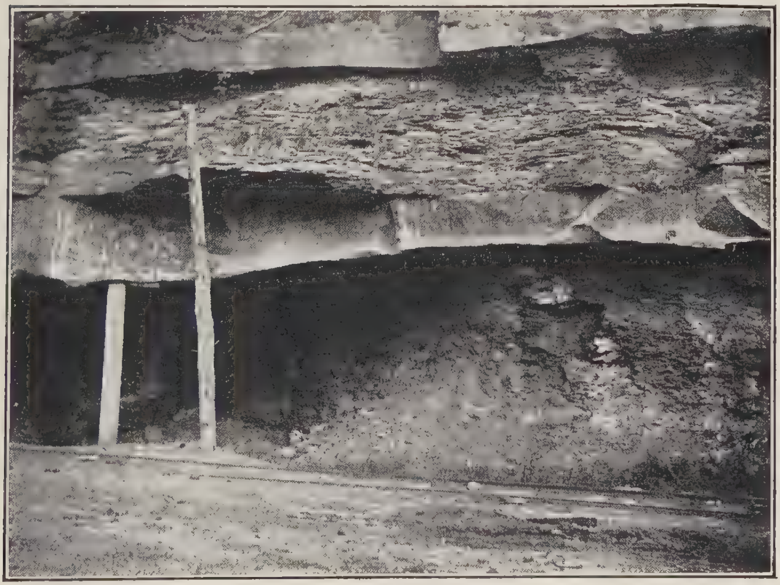

FIG. 167.—Shale-bed of Mahoning horizon, Charleston, W. Va. The shale is blue and red with some fire-clay mixed through it. (After Grimsley, W. Va. Geol. Surv., III, 1906.)

Monongahela series.—A series of coals, limestones, sandstones, and shales are included in this group, the general section being well exposed in Pinnickinnick Hill at Clarksburg. The Pittsburg coal at the base of the Monongahela is an important and well-recognized horizon. At Clarksburg the shales underlying and overlying this coal-seam are worked for building- and paving-brick.

The shales worked near Spilman for paving-blocks and building-brick lie near the top of the Monongahela series, and those at Moundsville are also near this horizon.

Dunkard or Permo-carboniferous.—The rocks of this age cover a belt 40 to 60 miles wide, bordering the Ohio River. They include a number of utilizable shales, and at present they are being worked at Parkersburg, Wood County, for making roofing-tile.

ANALYSES OF WEST VIRGINIA CLAYS

	I.*	II.	III.	IV.	V.	VI.
Silica (SiO_2)	54.35	57.75	58.78	56.3	61.44	52.24
Alumina (Al_2O_3)	21.49	20.17	22.57	19.07	26.18	29.28
Ferric oxide (Fe_2O_3)	8	7.00	4.13	9.58	0.30	2.73
Ferrous oxide (FeO)	....	0.33	1.40	....	0.36	0.51
Lime (CaO)	0.30	0.22	0.18	0.69	0.12	0.68
Magnesia (MgO)	0.79	1.22	1.00	2.01	....	0.2
Soda (Na_2O)	trace	0.62	0.54	....	0.02	0.37
Potash (K_2O)	6.35	2.59	3.15	....	....	2.11
Titanic oxide (TiO_2)	0.86	0.87	1.03	0.71	1.39	1.2
Moisture	1.62	2.75	1.05	....	0.77	1.28
Phosphoric acid (P_2O_5)	0.09	0.09	0.35	....	0.01	0.07
Sulphur trioxide (SO_3)	trace	....	....	....	....	....
Ignition	5.70	5.94	5.43	8.01	9.07	10.12
Total	99.55	99.55	99.61	96.37	99.66	100.79

	VII.	VIII.	IX.	X.	XI.	XII.
Silica (SiO_2)	57.58	59.76	57.52	57.89	66.69	56.19
Alumina (Al_2O_3)	21.41	22.79	21.76	21.59	21.83	26.31
Ferric oxide (Fe_2O_3)	3.75	0.60	3.41	5.62	0.37	2.82
Ferrous oxide (FeO)	3.45	3.53	3.7	1.26	1.00	0.96
Lime (CaO)	0.46	0.59	0.60	0.61	0.33	0.39
Magnesia (MgO)	1.44	1.23	0.88	1.55	0.10	1.44
Soda (Na_2O)	0.1	0.42	0.03	0.29	0.08	0.50
Potash (K_2O)	3.14	3.79	3.57	3.28	0.48	3.90
Titanic oxide (TiO_2)	0.84	0.82	0.83	0.72	1.11	0.63
Moisture	0.38	0.54	0.86	1.27	0.99	1.39
Phosphoric acid (P_2O_5)	0.11	0.46	0.14	0.21	trace	trace
Sulphur trioxide (SO_3)	....	....	....	....	....	....
Ignition	7.25	5.23	7.27	6.18	7.13	5.48
Total	99.91	99.79	100.57	100.47	100.11	100.01

* For references see foot of table following.

ANALYSES OF WEST VIRGINIA CLAYS—*Continued*

	XIII.	XIV.	XV.	XVI.	XVII.
Silica (SiO_2)	55.63	58.28	50.80	68.42	63.88
Alumina (Al_2O_3)	20.76	21.26	19.47	16.38	17.18
Ferric oxide (Fe_2O_3)	3.94	1.87	8.83	3.05	5.72
Ferrous oxide (FeO)	4.17	3.37	1.9	1.89	0.50
Lime (CaO)	0.86	0.78	1.51	0.94	0.16
Magnesia (MgO)	1.70	1.35	1.74	1.8	1.3
Soda (Na_2O)	0.34	0.39	0.89	0.63	0.6
Potash (K_2O)	2.97	2.87	2.24	0.93	2.29
Titanic oxide (TiO_2)	0.98	0.86	0.68	0.88	0.87
Moisture	1.03	1.30	0.6	......	1.76
Phosphoric acid (P_2O_5)	0.23	0.39	0.2	0.08	0.36
Sulphur trioxide (SO_3)	trace	......	......	......	......
Ignition	6.98	6.84	11.37	4.58	5.60
Total	99.59	99.56	100.23	99.58	100.22

PHYSICAL TESTS OF WEST VIRGINIA CLAYS

	I.	II.	III.	V.	VI.	VII.	VIII.
Water required, per cent	......	28	25	2.1	28	24	26
Tensile strength, lbs. per sq. in.	......	122	34	32	58	40	46
Air-shrinkage, per cent	......	4	3.5	3	4	4	4
Cone of incipient vitrification	......	1	......	......	......	1	1
Cone of vitrification	5	5	1	......	26	5	5
Cone of viscosity	......	......	5+	30+	28		
Fire-shrinkage, per cent	......	11	10	......	2	6	6
Color when burned	red	......	red	buff	buff	brown	brown

	IX.	X.	XI.	XII.	XIII.	XIV.	XVII.
Water required, per cent	26	27	20	24	22	25	32
Tensile strength, lbs. per sq. in.	40	36	75 to 90	89 to 100	109	78	140
Air-shrinkage, per cent	3.5	4	4	4	4.5	4.5	6
Cone of incipient vitrification	1	1	......	1	......	1	1
Cone of vitrification	5	5	30	5	1	5	5
Cone of viscosity	......	......	......	......	5		
Fire-shrinkage, per cent	10	8	0	6	2	.7	12
Color when burned	red	red	buff	red	red	red	red

I. Residual limestone clay, Charlestown, Silurian.
II. Residual shale-clay, Martinsburg, Silurian.
III. Shale, Elkins, Randolph County, Hamilton.
IV. Shale, Decker's Creek near Morgantown, Mauch Chunk.
V. Fire-clay, Piedmont, Mount Savage clay.
VI. Flint-clay
VII. Gray shale } Clifton Mine, New Cumberland, Middle Kittanning.
VIII. Blue shale
IX. Clay
X. Shale } Ætna mine, New Cumberland, Lower Kittanning.
XI. Flint-clay
XII. Plastic clay } Thornton, in Conemaugh series, Mahoning coal horizon.
XIII. Shale, Morgantown, Pittsburg red shale.
XIV. Blue shale, Huntington, Conemaugh series.
XV. Mixture of Spilman shales, Spilman, Conemaugh series.
XVI. Parkersburg, Dunkard shale.
XVII. River-clay, Parkersburg, Pleistocene.

Nos. I–XVII selected by Dr. Grimsley as representative ones, from Vol. III, W. Va. Geol. Surv.

Pleistocene

A number of brick plants in the State obtain their raw material from deposits near creeks or rivers. These clays underlie terraces and occur either near the present river-level or a number of feet above it. The former are flood-plain deposits built up by the rivers in recent times, while the latter represent the remnants of lake-beds formed when the valleys were dammed by ice, thus giving rise to the formation of temporary lakes. The clays of the Monongahela, Teays, and adjacent valleys are of the second type.

REFERENCES ON WEST VIRGINIA CLAYS

1. Grimsley, G. P., The Clays of West Virginia, W. Va. Geol. Surv., III, 1906.
2. White, I. C., Clays of West Virginia, The Ceramist, VII, p. 254, 1926.

WISCONSIN

In this State the clay-deposits belong to formations representing somewhat the two extremes of the geological column. Those belonging to the older formations are nearly all of residual character, while those belonging to the sedimentary deposits are of very recent geologic age. It seems best, therefore, to divide them into two groups, namely, the residual clays and the sedimentary clays.

Residual Clays

These have been derived from a variety of rocks, including granites and gneisses, greenstones and allied volcanic rocks, limestone and dolomite, sandstone and shale.

Pre-Cambrian residuals.—These occur at a number of points in the central part of the State, in Eau Claire, Jackson, Wood, Portage, Marathon, and Clark counties. They are usually gritty clays which have been formed by the decomposition of schists or gneisses, and vary in depth from perhaps 2 to 3 feet to as much as 40. Although sometimes reaching nearly to the surface, they are at other times covered by a bed of Potsdam sandstone which has apparently protected them from erosion. Deposits of this occur in the vicinity of Grand Rapids, Eau Claire, Black River Falls, Stevens Point, Abbotsford, etc. They are nearly all red-burning, and while refractory ones low in iron are known to occur, the deposits of them so far as found are rather small. Their main use is for the manufacture of common brick, but at Halcyon near Black River Falls the material has been found adapted to the manufacture of dry-press brick and even paving-brick.

Potsdam shales.—In a few localities there occurs at the base of the Potsdam a tough plastic clay which has been derived by the weathering of a siliceous shale. This material has been exposed near Merrillan, Durand, and other points, but has not been utilized to any extent for he manufacture of clay-products.

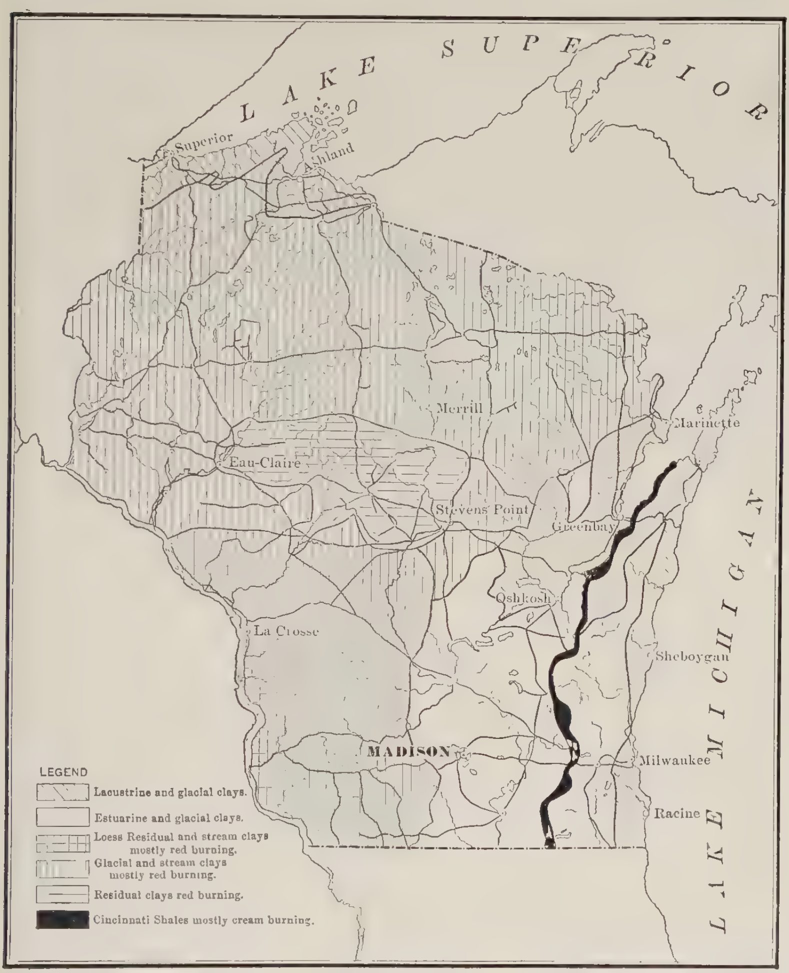
LAKE SUPERIOR
Superior
Ashland
Merrill
Marinette
Eau-Claire
Stevens Point
Greenbay
Oshkosh
La Crosse
Sheboygan
MADISON
Milwaukee
Racine
LAKE MICHIGAN
LEGEND
Lacustrine and glacial clays.
Estuarine and glacial clays.
Loess Residual and stream clays mostly red burning.
Glacial and stream clays mostly red burning.
Residual clays red burning.
Cincinnati Shales mostly cream burning.

FIG. 168.—Map of Wisconsin, showing distribution of clay-bearing formations. (Adapted from Buckley, Wis. Geol. and Nat. Hist. Surv., Bull. VII, 1901.)

Ordovician limestone residuals.—Within the driftless area of Wisconsin the cherty galena limestone is found weathered in its upper

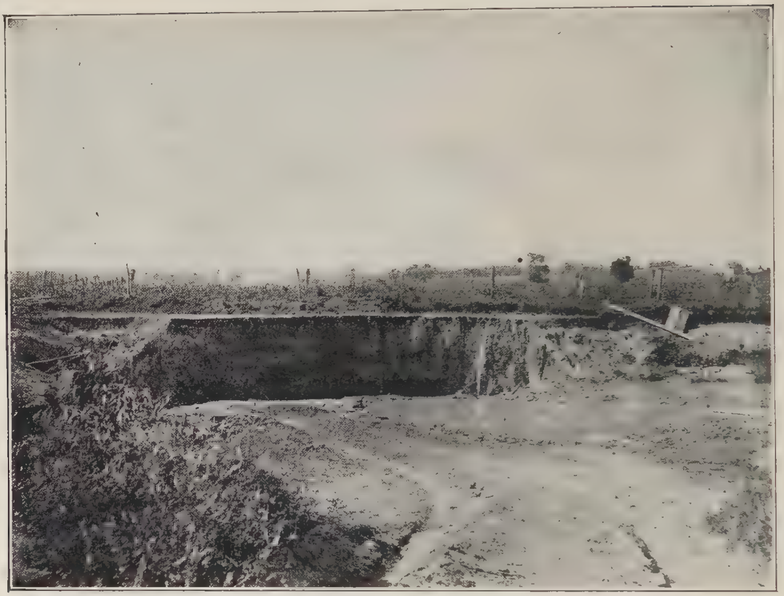

Fig. 169.—Pit of estuarine clay, Fort Atkinson, Wis. The flat area is underlain by clay, while the surrounding low hills are of sand. (Photo by H. Ries.)

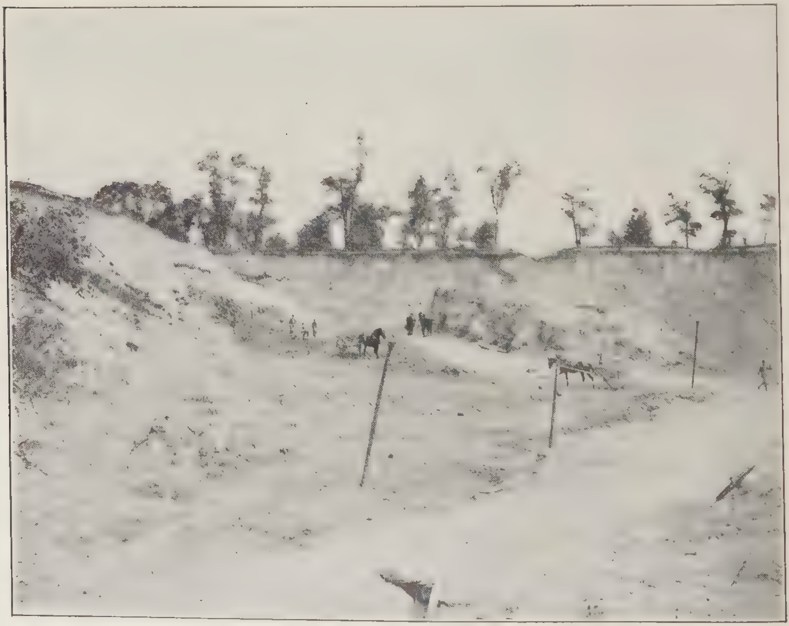

Fig. 170.—Pleistocene brick-clay, Milwaukee, Wis. The mound in middle of pit is sand and is left standing. (Photo by H. Ries.)

portion to sandy residual clay containing many flint fragments scattered through it. Up to the present time it has not been used for the manufacture of common brick to which it is chiefly adapted, nor is there any likelihood of its ever becoming of any importance.

SEDIMENTARY CLAYS

Hudson River shale.—This shale forms a narrow belt in the eastern part of Wisconsin which extends from the southern boundary of the State up to Green Bay. In this State it is not very well adapted to the manufacture of brick, but on weathering breaks down rather easily to a yellow clay which has very fair plasticity and is usually red-burning. The material has been worked at Stockbridge, Calumet County, and at Oakfield, Fond du Lac County, for the manufacture of brick. At the former locality a mixture of the weathered shale and the partly weathered material is used with excellent results. A second area of these shales is known to occur in Lafayette County, to the east and southeast of Platteville, where the material is to be found around the base of the Mound Hills so prominent in that region. It weathers to a yellow clay of high plasticity and one which burns to a very hard body of excellent red color.

PLEISTOCENE CLAYS

The Pleistocene clays of Wisconsin have been grouped by Buckley (Ref. 1) as follows: 1. Lacustrine deposits; 2. Stream deposits; 3. Estuarine deposits, and 4. Glacial clays.

Lacustrine deposits.—These represent a very extensive type, and were laid down during the former inland extension of the Great Lakes, so that they are now often found some distance from the present lake shore. Thus, around Racine, they occur 18 miles inland. They are also found at Sheboygan, over parts of Door County, and in parts of Manitowoc, Calumet, and Fond du Lac counties; much of Green Lake, Waushara, and Waupaca counties too are underlain by them, while to the north they are found as far as Shawano. These lacustrine deposits, adjoining Lake Michigan on the east and Lake Superior on the north, are an important source of cream-burning brick-clays, and the beds often exceed 100 feet in thickness. Sometimes the upper few feet burn red, owing to the fact that the carbonate of lime has been leached out of them. Around Green Bay, Manitowoc, and Racine these clays are much used for the manufacture of common, pressed brick, and drain-tile, but they are of little value for anything else.

Estuarine clays.—These include all the clays of eastern Wisconsin which are underlain by limestone and have been modified by glacial action. They were formed at the same time and in association with the lake-deposits, but differ from them usually in showing a more variable lime-content and burn hard and dense at a lower temperature. Thus, for example, the lake-clays apparently have to be burned up to cone 3, while the estuarine clays can be burned at cone 05 to 1. These estuarine deposits are found along the Fox, Wolf, Rock, Wisconsin, Eau Claire, Chippewa, Black, Red, Cedar, and many other rivers in the eastern, northeastern, and southern parts of the State.

ANALYSES OF WISCONSIN CLAYS

	I.	II.	III.	IV.	V.
Silica (SiO_2)	64.50	62.59	35.93	48.39	44.18
Alumina (Al_2O_3)	26.20	17.42	11.75	12.50	10.83
Ferric oxide (Fe_2O_3)	0.07	5.88	4.08	5.40	3.30
Lime (CaO)	....	none	12.43	10.88	14.05
Magnesia (MgO)	....	1.24	9.92	4.82	5.91
Potash (K_2O)	0.31	8.08	2.46	3.90	3.10
Soda (Na_2O)	....	0.52	1.24	0.68	0.70
Loss on ignition	8.90	4.15	22.06	13.02	17.34
Titanic acid (TiO_2)	....	0.30	0.30	0.43	0.30
Manganese oxide (MnO_2)	....	SO_3 trace	0.10	trace	

	VI.	VII.	VIII.	IX.	X.
Silica (SiO_2)	40.17	31.90	71.77	65.44	69.86
Alumina (Al_2O_3)	9.14	8.74	13.74	13.51	13.55
Ferric oxide (Fe_2O_3)	3.00	3.00	3.60	5.40	5.46
Lime (CaO)	14.49	17.06	1.23	2.95	0.71
Magnesia (MgO)	8.34	10.63	1.17	2.20	1.43
Potash (K_2O)	3.06	2.20	2.30	3.44	2.36
Soda (Na_2O)	0.34	0.82	1.20	1.54	1.78
Loss on ignition	21.37	25.19	5.00	4.69	4.40
Titanic acid (TiO_2)	0.35	0.25	0.45	0.60	0.77
Manganese oxide (MnO_2)	0.09	0.19	trace	trace	trace

LOCALITIES OF THE ABOVE

No.	Locality.	Geological Age.	Uses.
I.	Hersey	Residual	Not worked
II.	Merrillan	Potsdam	" "
III.	Oakfield	Hudson	Common brick
IV.	Green Bay	Pleistocene	Brick
V.	" "	"	"
VI.	Milwaukee	"	"
VII.	Watertown	"	"
VIII.	Chippewa Falls	Glacial	"
IX.	Menomonie	"	Pressed brick
X.	Whittlesey	"	Brick

Nos. I–X from Wis. Geol. and Nat. Hist. Surv., Bull. 7, 1901.

Glacial clays.—These have been deposited over a large part of the northern half of the State and include a series of deposits of uncertain extent and variable character and thickness. In some places they consist of bowlder-clay and are therefore of a very stony character, while at others they may represent deposits that have been formed in temporary lakes during the last glacial epoch. Those worked at Athens belong to the former type, and those worked at Menomonie and forming the basis of an extensive local industry belong to the latter type. Under this heading we should perhaps also include the silty loess-clays which cover a large area in the western part of the State and are worked at Platteville, Menomonie, La Crosse, and other places. They represent a good character of clay, which in many instances is used only for common brick, but is also adapted to the manufacture of dry-press brick.

REFERENCES ON WISCONSIN CLAYS

1. Buckley, E. R., The Clays and Clay Industries of Wisconsin, Wis. Geol. and Nat. Hist. Surv., Bull. 7, Pt. I, 1901.
2. Chamberlin, T. C., Geol. of Wis., I, p. 669.
3. Irving, R. D., On the Kaolins of Wisconsin, Wis. Acad. Arts and Letters, Trans., 1876.
4. Irving, R. D., Geol. Wis., II, p. 630.
5. Irving, R. D., Mineral Resources of Wisconsin, Amer. Inst. Min. Eng., Trans., VIII, p. 478.
6. Ries, H., The Clays of Wisconsin and their Uses, Wis. Geol. and Nat. Hist. Surv., Bull. 15, 1906.
7. Sweet, E. T., Milwaukee Clay, Amer. Jour. Sci., iii, XXIV, p. 154.

WYOMING

Little is known regarding Wyoming clays, owing largely to their lack of development. W. C. Knight says:[1] "So far as is known, the clays of Wyoming that have any commercial importance occur in beds of the sedimentary rocks. These clay-beds are most numerous in the Jurassic and Cretaceous formations, but are found to some extent in the Tertiary." The formations containing these clays are found flanking nearly all of the mountain-ranges in the State, and the clay-beds vary in thickness from 4 to 40 feet. Bowlder-clays, that are so common in the East, are not known and will be found only in small and isolated localities. With the exception of the manufacture of common brick no attention has been paid to any of the clay industries, and all of the fire-clay goods used in Wyoming are manufactured in Colorado, while pressed brick are shipped in from various points. This condition is largely due o the limited population of the State, and the slight demand for clay-products. The common brick which are, as a rule, manufactured from loess, are very siliceous and fragile, although in a few places there is clay enough in the loess to make a medium-grade brick. Judging from the appearance of the clay-beds and their geological position, they will, when tested, prove equal to the Colorado beds.

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[1] Eng. and Min. Jour., LXIV, p. 546, 1898.

At Cambria, Weston County, the clays associated with the coals have been found adapted to the manufacture of dry-press brick.

Bentonite.—A peculiar variety of clay found in Wyoming and known as *bentonite* was first described by W. C. Knight under the name of *taylorite*.[1] Finding that the latter name was preoccupied, he proposed the name of bentonite for it [2] from its occurrence in the Benton formation. The deposits in the northeastern part of the State, in the vicinity of Newcastle, were first described in detail by N. H. Darton.[3]

Bentonite when fresh has a yellowish-green color, but assumes a light cream tint on exposure. It is fine-grained, soft, and absorbs three times its weight of water, accompanied by swelling. Its specific gravity is 2.18. Professor Knight pointed out its resemblance to the *ehrenbergite* of Germany, but it differs from it in containing less alkali. The soda reported in the analyses is, as a rule, found in the clay in thin seams as sodium sulphate. T. T. Read thought, from analyses examined by him, that it most closely resembled *montmorillonite* (Ref. 8).

It will be seen from the analyses given below that the clay shows a somewhat variable composition, and that its peculiar properties are due no doubt to physical rather than chemical conditions.

ANALYSES OF BENTONITE

	I	II.	III.	IV.	V.	VI.
Silica (SiO_2)	59.78	61.08	63.25	65.24	64.0	60.18
Alumina (Al_2O_3)	15.10	17.12	17.62	15.88	22.9	26.58
Ferric oxide (Fe_2O_3)	2.40	3.17	3.70	3.12	3.1	
Lime (CaO)	.73	2.69	4.12	5.34	1.0	.23
Magnesia (MgO)	4.14	1.82	3.70		2.0	1.01
Potash (K_2O)	......	......	......	......	......	1.23
Soda (Na_2O)	......	.20	......	......	......	
Sulphur trioxide (SO_3)	......	0.80	1.53			
Water (H_2O)	16.26	12.10	und. ?	9.17	7.0	10.26
Total	98.41	98.98	93.92	98.75	100.0	99.49
Specific gravity	2.18	......	2.132			

I. Rock Creek, }
II. Crook County, } Wyoming Exper. Sta., Bull. 14 p. 193, 1893.
III. Weston County, }
IV. Natrona County, } W. C. Knight, analyst.
V. Cosgriff. J. Ogden, analyst. U. S. Geol Surv., Bull. 285, p. 446.
VI. Cassa Mining Co., T. T. Read, analyst. U. S. Geol. Surv., Bull. 285, p. 446.

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[1] Eng. and Min. Jour., LXIII, p. 600, 1898.

[2] Ibid., LXVI, p. 491.

[3] Geologic Atlas, Folio 107, 1904.

The peculiarity of composition of this clay lies in its high combined water-content as compared with the alumina percentage.

The clay, which occurs mainly in the Benton group of the Cretaceous, and some in the Niobrara, has been found extensively in Wyoming in Crook, Johnson, Weston, Converse, Natrona, Carbon, Albany, and Laramie counties. More recently additional deposits have been discovered 8 miles east of Frannie, and 5 miles north of Cowley, Wyoming.[1] The distribution of the Benton formation in Wyoming is shown in Fig. 171.

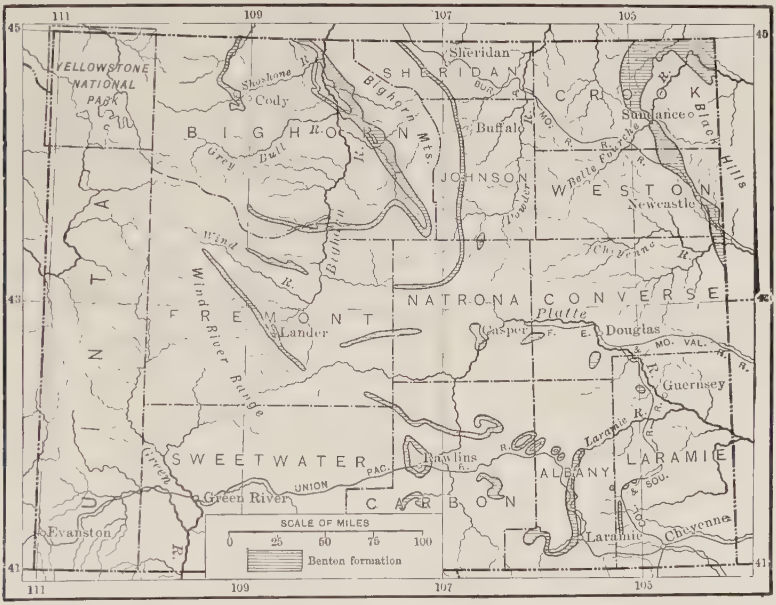

FIG. 171.—Map of Benton formation in Wyoming. (After Fisher, U. S. Geol. Surv., Bull. 260.)

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[1] U. S. Geol. Surv., Bulls. 260, 562, 1905.

CHAPTER X

CANADA[1]

CLAYS are widely distributed in the Dominion of Canada, and are locally developed at a number of points, where there are suitable markets within reach. The wares produced not only supply the domestic demand, but are also exported to some extent.

The statistics for 1924 given below are taken from the Annual Report of the Dominion Bureau of Statistics.

PRODUCTION OF CLAY PRODUCTS IN CANADA FROM DOMESTIC CLAYS, 1924

Kind	I	II
Brick: Soft mud process { Face . . . . . . M	10,831	$185,248
Brick: Soft mud process { Common . . . . . . M	50,079	746,044
Stiff mud process (wire cut) { Face . . . . . . M	80,565	1,842,224
Stiff mud process (wire cut) { Common . . . . . . M	124,556	1,880,631
Dry press { Face . . . . . . M	35,203	761,572
Dry press { Common . . . . . . M	12,794	168,043
Fancy or ornamental brick (including special shapes, embossed and enamelled brick) . . . . . . M	755	98,460
Sewer brick . . . . . . M	2,690	40,775
Firebrick from domestic clay . . . . . . M	4,327	209,256
Fireclay . . . . . . Ton	3,645	26,258
Fireclay blocks and shapes	. . . .	51,273
Structural tile: Hollow blocks (including fireproofing and load-bearing tile) . . . . . . Ton	96,818	926,777
Roofing tile . . . . . . No.	7,377	917
Floor tile (quarries) . . . . . . Sq. ft.	444,601	35,608
Drain tile . . . . . . M	15,137	409,369
Sewer pipe (including copings, flue linings, etc.) . . . . . . Ton	76,355	1,594,280
Pottery, glazed or unglazed	. . . .	238,242
Total	. . . .	$9,215,077

I. Quantity. II. Total selling value.

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[1] The author is indebted to Messrs. J. McLeish, H. Frechette and Prof. J. A. Allan for much recent information regarding Canadian clays.

IMPORTS OF CLAY AND CLAY PRODUCTS IN CANADA, 1924

		Quantity	Value
Building brick	M	5,425	$124,983
Building blocks	M	......	63,559
Clays: China	Cwt.	390,613	250,113
Fire	Cwt.	886,091	186,696
Pipe			847
Other clays			56,590
Drain tile, unglazed			3,014
Drain and sewer pipe			68,449
Earthenware and chinaware			4,124,607
Fire-brick			1,119,840
Paving-brick			69,493
Other clay manufactures			842,577

EXPORTS OF CLAY AND CLAY PRODUCTS FROM CANADA, 1924

Building brick	$38,105
Clay: Unmanufactured	1,127
Manufactures	109,295
Earthenware	72,839
Porcelain insulators	322,206

VALUE OF CLAY PRODUCTS BY PROVINCES, FROM DOMESTIC CLAY, 1924

	Value sold or used	Per cent total value
Prince Edward Island	$3,340	.04
Nova Scotia	355,948	3.86
New Brunswick	74,994	.81
Quebec	2,435,695	26.44
Ontario	5,089,299	55.24
Manitoba	117,450	1.27
Saskatchewan	137,280	1.49
Alberta	540,477	5.86
British Columbia	460,594	4.99
	$9,215,077	100.00

The clay resources are taken up below by provinces.

ALBERTA

Clay-bearing formations.—These include the Cretaceous, Tertiary, and Pleistocene. The first two contain vast supplies of shales and clay shales, some of which are of excellent quality but they are little utilized.

CRETACEOUS

Approximately four-fifths of Alberta is underlain by Cretaceous formations which are covered almost entirely by Pleistocene deposits, with Lower Tertiary in a narrow central belt. Within the front ranges of the Rocky Mountains in the western part of the Province, and within the more disturbed foothill belt of Alberta, there are also outcrops of Cretaceous beds.

LOWER CRETACEOUS

Kootenay shale.—This is the oldest Cretaceous shale formation in Alberta and outcrops along the eastern edge of the Rocky Mountains and within the front ranges. It is a silicious, ferruginous red-burning shale which has been used at Blairmore for common brick, but has not been sampled elsewhere in the Province.

The McMurray formation on the Athabaska River below Fort McMurray has non-calcareous, plastic clay-beds interstratified with the bituminous sand. This clay is semi-refractory, fusing at cone 18. The raw material has been carved into ornaments and curios, and its utilization in this form is promising. The overlying Clearwater shales are suitable for stiff-mud brick.

UPPER CRETACEOUS

Colorado.—This formation consists largely of shale and is over 1500 feet in thickness. It outcrops along the foothills of Alberta and in places these marine shales have formed residual clays. The lower members in this formation, exposed on the McLeod River near Cadomin, are used in the Edmonton Portland Cement plant at Marlboro. The upper members of the Colorado in the Bow Valley, close to the front of the mountains, are utilized by the Canada Cement Company at Exshaw. These marine shales from the Crowsnest district west of Pincher Creek and Passburg have been proven by tests to be suitable for brick-making.

Belly River series.—On account of the trough-like structure extending north and south through Alberta the members of this series outcrop in the eastern part of the Province, and also in the foothills to the west. In the plains region the formations making up the Belly River series are best exposed in the banks of the larger rivers, such as the North and South Saskatchewan (Fig. 172), Red Deer, Bow, and Belly Rivers, where some splendid sections are to be seen. The character of these shales may be summed up as follows: (1) Usually red-burning. (2) Often very plastic. (3) Occurrence somewhat lens-like, but individual lenses

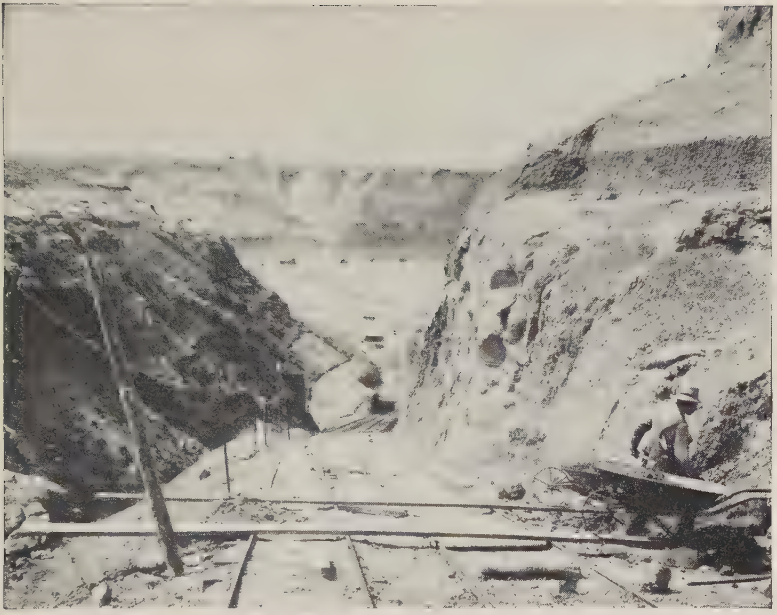

Fig. 172.—Bluffs in Belly River shales along South Saskatchewan River, north of Medicine Hat, Alberta. (H. Ries, photo.)

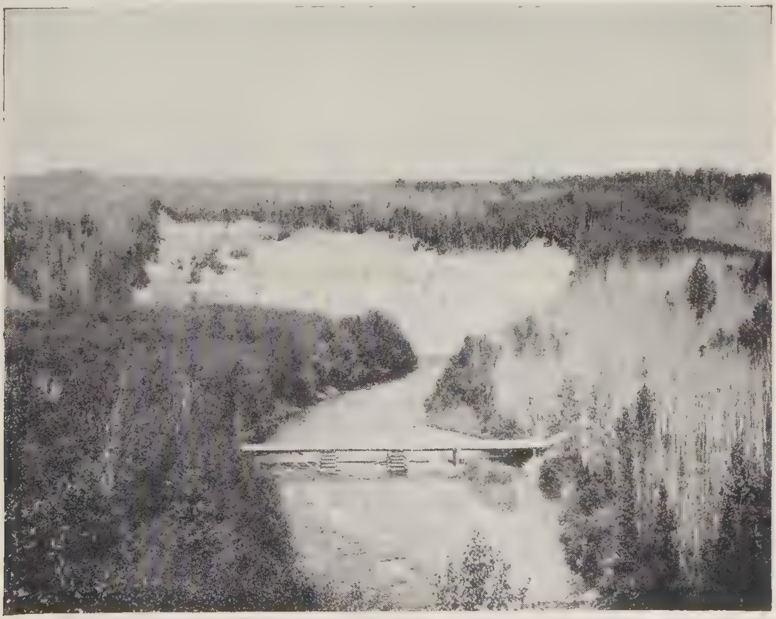

Fig. 173.—Exposures of Edmonton shale near Entwhistle, Alberta. (H. Ries, photo.)

often very large. (4) Fusion-point usually not higher than cones 5 or 6. (5) Many work smoothly through a die. (6) Careful drying is commonly necessary to prevent cracking.

The Belly River shales are worked at Redcliff (Fig. 172), near Medicine Hat. The main product being common brick, although dry-pressed face brick and hollow blocks have also been made. A rough cut " tapestry-like " brick is now being manufactured and is used extensively throughout the province. The clays at Dunmore are also employed for fireproofing and pressed brick. Residual clays from the Belly River shales are worked at Smoky Lake.

Bearpaw shales.—These marine shales have a wide distribution in southeastern Alberta and frequently form residual clays. The formation has a maximum thickness of about 600 feet, but it thins to the north and disappears in the Edmonton district. It also thins out towards the west, and does not occur as marine shale in the foothills. Some of the beds are gypsiferous. Tests made on these shales at Irwin indicate that in this region at least the shale is not even suitable for common brick.

Edmonton formation.—A broad belt of this formation extends through the central part of the Province, south from Lesser Slave lake and narrowing to a belt about 15 miles wide at the southern boundary. The formation outcrops along the eastern and western sides of this belt, as it is overlain by younger Tertiary rocks. The formation is 1100 feet thick on the Red Deer River, and consists of clay shales, sandstones and coal seams. Many of the shales are bentonitic, and this decreases their usefulness in the manufacture of clay products, as it gives trouble in drying and burning. Some of the best-known deposits suitable for hollow ware and possibly paving-brick occur along Pembina River west of Edmonton (Fig. 173).

Tertiary

Paskapoo shales.—The Tertiary beds overlie the Edmonton formation and extend as an irregular belt with a maximum width of 90 miles north and south through the central part of the Province from the Athabaska River to the southern boundary. The section consists of alternating shales and sandstones. Except along the rivers, outcrops are scarce on account of the veneer of Pleistocene and younger deposits. Much of the shale is too sandy or calcareous, but the formation contains a number of shale deposits suitable for common or pressed brick and tile, sometimes glazed and fireproofing. The shales are red-burning, with fusion-points ranging from cone 3 to cone 15. They are used on a small scale for brick and tile at Calgary.

PLEISTOCENE (RECENT)

This is the surface formation in most of the Great Plains region, and the clays found in it are more widely used than the Cretaceous and Tertiary shales. The surface clays may be divided into (1) Lake clays; (2) River terrace and flood plain deposits; and (3) Delta deposits.

The Edmonton lake clays are used for common and pressed brick and are found to be most suitable. Sandy, laminated, calcareous lake clays are used for common brick at Red Deer. Flood-plain clays are employed for common and dry-pressed brick, and are plastic, gritty clays which burn to a light red at cone 03, but the brick is very porous.

In general the surface clays are silty and yield a porous brick, but they are used because they are easy to work.

PHYSICAL TESTS OF ALBERTA CLAYS

		I	II	III	IV	V
Water plasticity, per cent		28	25	19	25	22
Linear air shrinkage, per cent		10.4	8.2	6.0	6.9	4.8
Tensile strength, pounds per square inch		270	335	165	176	381
Cone 010	Linear fire shrinkage, per cent	0.2	0.2	0.4	0.8	slightly swelled
	Absorption, per cent	14.24	16.63	14.90	19.34	14.62
Cone 03	Linear fire shrinkage, per cent	3.7	2.0	2.3	1.0	3.0
	Absorption, per cent	9.23	11.02	9.46	18.47	6.02
Cone 1	Linear fire shrinkage, per cent	4.3	4.6	....	....	5.0
	Absorption, per cent	0.28	0.0	....	....	0.0
Cone of fusion		6	5	1	1	5

I. Shale, Edmonton.
II. Surface clay, Edmonton.
III. Shale, Brickburn.
IV. Shale, Red Deer.
V. Shale, Entwhistle. At cone 3, fire shrinkage 6, and absorption 0.

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BRITISH COLUMBIA

Clay-bearing formations.—These include deposits of residual, Cretaceous, Tertiary, Pleistocene, and Recent age. The development of most of these is comparatively limited.

Residual

None of the residual clays have been utilized commercially, nor are they abundant. Attempts are being made at present to develop deposits at Williams Lake and on Vancouver Island, and small quantities of brick have been marketed. At Kyuquot in the northwest part of Vancouver Island, there is a deposit of residual clay derived probably from rhyolite. It is said to be refractory and white-burning, but nothing definite is known regarding its extent.

Residual clays from volcanic rocks are also noted from Kamloops Lake, but they are not used.

Mountain Region

In the mountain region of British Columbia most of the shales (Cretaceous and Tertiary) are either too siliceous or too much metamorphosed to be of any value for clay products. In the Nicola Valley and at a few other localities there are shales which could be used for brick, but none of refractory quality have been found.

In the larger valleys in the mountains there are surface deposits of lake and flood-plain clays. One of the most extensive is in the Nicola Valley between Merritt and Nicola, and could be used for brick and tile. At several points in the Okanagan Valley there are deposits which are used for brick-making.

Pacific Coast Region

Tertiary.—The shale deposits of this region are less extensive than the surface clays. Tertiary shales occur around Nanaimo and Comox on Vancouver Island, but they are usually too sandy or carbonaceous to be used alone. Some have been employed for brick-making, and they have also been utilized in a sewer-pipe mixture.

The most valuable deposits of shale and clay are those which occur in Sumas Mountain near Clayburn. The section here, which is part of the Eocene delta of the Frazer River, shows a series of shales and clays, interbedded with coals, sandstone and conglomerate. Underground methods are employed for working the clays, which are adapted to the manufacture of pressed brick, paving-brick, fire-brick, fireproofing, sewer-pipe, and roofing-tile.

On Blue Mountain near Whonnock there are other deposits of shale and clay which may become of considerable importance in the future.

Pleistocene.—The Pleistocene clays include the following groups: (1) Plastic, red-burning surface clays of the lower Frazer River Valley, worked for brick and tile at New Westminster, Port Haney, Ruskin, etc.; (2) glacial clay on southern Vancouver Island and the islands between it and the mainland, of red-burning character, and worked for brick and structural-tile; (3) glacial clay deposits along the coast near Prince Rupert, which are gritty but plastic, and suitable for brick and drain-tile.

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MANITOBA

Clay-bearing formations.—Under this head are to be included only deposits of Cretaceous and Pleistocene age. The Silurian and Devonian formations occupy a large area south and west of Lake Winnipeg, but are mostly limestone. The few shales from them which have been tested have not proved to be of any value.

Cretaceous

The Cretaceous shale formations in Manitoba are the Niobrara and the Pierre.

The Niobrara underlies a large area in southern and western Manitoba while the Pierre occupies the summit of all the higher land in the western part of the province.

In southern Manitoba the Niobrara shale is very plastic and somewhat carbonaceous. It is used at Leary for dry-pressed brick.

The upper part of the Pierre is more valuable than the lower, being made up in large part of hard, light-gray, fine-grained shale. It has too low a plasticity when used alone, and does not burn dense enough. Pressed brick have been made from it at La Rivière.

PLEISTOCENE

These are surface clays, all of which are more or less calcareous, often silty, and tend to check in air-drying. They may be divided according to their origin into: (1) Lake clays, (2) River-terrace or flood-plain deposits, and (3) Delta deposits.

Around Winnipeg where there is located an important brick industry in the western provinces the clays are of two types, viz.: (1) A calcareous surface clay, which lies immediately below the surface, and is 4 to 5 feet thick. It is probably a flood-plain silt of the Red and Assiniboine rivers; (2) A tough, sticky under-clay, probably a deposit of Lake Agassiz, and not used because it cracks and warps in the kiln.

All the brick plants around Winnipeg use the calcareous surface clay which is cream to buff burning, the products being common and hollow brick. The industry here is less important than formerly.

PHYSICAL TESTS OF MANITOBA CLAYS

		I	II	III	IV
Water plasticity, per cent		37.8	32.0	28.2	39.0
Linear air shrinkage, per cent		4.9	9.2	4.5	10.3
Tensile strength, pounds per square inch		113	349	240	248
Cone 010	Linear fire shrinkage, per cent	2.4	0.6	−2.5	3.7
	Absorption, per cent	28.73	15.21	31.44	13.31
Cone 03	Linear fire shrinkage, per cent	4.0	9.6	−2.4	3.4
	Absorption, per cent	24.45	0.21	31.42	vit.
Cone 1	Linear fire shrinkage, per cent	5.0	3.0	−2.4	....
	Absorption, per cent	19.54	0.65	28.37	....
Fusion point, cone		....	5	5	....

I. Pierre shale, Riding Mountain.
II. Niobrara shale, Leary.
III. Surface clay, Winnipeg.
IV. Under clay, Winnipeg.
All from Can. Geol. Surv., Mem. 24-E.

REFERENCES ON MANITOBA CLAYS

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NEW BRUNSWICK

Clay-bearing formations.—The only clay- or shale-bearing formations in this province which are likely to contain workable deposits are the Carboniferous and Pleistocene. The Carboniferous rocks underlie a roughly triangular area of rather low relief in the eastern part of the province, and also occur in two or three smaller patches farther west. The beds are nearly horizontal. The western and southern portions of the province are more rugged and underlain by igneous and pre-Carboniferous metamorphic rocks not likely to yield any commercial clay deposits.

Lower Carboniferous

The upper part of the Lower Carboniferous carries thick beds of red and greenish shales, in part of sandy character. Tests indicate that there are shales suitable for red building-brick and paving-brick.

Middle Carboniferous

In addition to several beds of shale, this member contains a thin seam of coal which is being worked at several points. The shale above the coal is most favorably located for development as part of it has to be removed with the coal in order to give head room, and there are already large accumulations of it on the waste dumps. This shale would make good common brick, and at three localities in the Grand Lake Coal area it has the requisite properties for making vitrified paving-block and sewer-pipe. Shales also occur below the coal. There are in addition some semi-refractory shales in this area.

Upper Carboniferous

Near Sackville in southeastern New Brunswick there is some shale that could be used for common brick but not vitrified ones.

PLEISTOCENE

The clays of this age consist of glacial boulder clay and stratified surface-clays. The latter were deposited along the coast and in the main valleys during a post-glacial depression and are found under terraces up to 200 and 300 feet above sea level. They are the most widely used of any of the clays found in the province, and make a good grade of common red brick.

PHYSICAL TESTS OF NEW BRUNSWICK CLAYS

		I	II	III	IV
		Per cent	Per cent	Per cent	Per cent
Water plasticity		15	24	....	22
Linear air shrinkage		4.8	6.6	6.5	7.0
Cone 010	Linear fire shrinkage	0.0	0.15	1.0	1.7
	Absorption	10.2	13.3	16.0	16.9
Cone 05	Linear fire shrinkage	2.6	....	3.0	....
	Absorption	4.6	....	3.0	....
Cone 03	Linear fire shrinkage	2.3	4.0	9.0	....
	Absorption	2.6	7.4	....	....
Cone 1	Liner fire shrinkage	2.3	5.0	....	....
	Absorption	0.8	0.8	....	....
Cone of fusion		3	5	1	....

I. } Shale, Grand Lake area.
II. }
III. Surface clay, St. Johns.
IV. Pleistocene marine clay, Chatham.
All from Can. Geol. Surv. Mem. 44.

REFERENCES ON NEW BRUNSWICK CLAYS

1. Keele, J., Clay and Shale Deposits of New Brunswick, Can. Geol. Surv., Mem. 44, 1914.
2. Keele, J., Grand Lake Coal Area, Can. Dept. Mines, Sum. Rept., 1921, pp. 254 and 259, 1922.
3. Ries, H., and Keele, J., The Clay and Shale Deposits of Nova Scotia and Portions of New Brunswick, Can. Geol. Surv., Mem. 16, 1911.

NOVA SCOTIA

Clay-bearing formations.—The formations likely to contain clay or shale deposits of value are the Lower Carboniferous, Coal-measures, Permian, Cretaceous, and Pleistocene. In many parts of Nova Scotia the bed-rock is metamorphosed or igneous and offers little of promise to the ceramic industry.

Lower Carboniferous

This underlies a rather extensive area in central Nova Scotia and another one in Cape Breton. There are some beds of shale interstratified with limestone which are suitable for common brick, and have been used at Pugwash. This shale works up to a smooth plastic mass with 22 per cent of water and fires to a hard body with low fire-shrinkage, good red color, and moderate absorption at cone 010.

The Millstone grit is mostly sandstone, the shale-beds being usually of small extent. Common brick shales in large enough bodies to be of commercial value have been found at a few localities as at Bailey Brook, Pictou County, and near Sydney.

Coal-measures

These contain the most important shale formations found in Nova Scotia, although the deposits are rarely of great extent and thickness. They are found around Sydney, but would be of value only for building-brick.

In the Pictou County coal field the Coal-measures contain a large amount of shale. One deposit of hard, smooth, carbonaceous material has been worked at New Glasgow for hollow block and sewer-pipe. Brick are manufactured at Westville from a hard grayish-black buff-burning shale of the Coal-measure.

Permian

The only known clay or shale deposits of importance in the Permian are found around Woodburn, east of New Glasgow. They could be used for common or face brick, but are not favorably located for extensive development.

Cretaceous

A curious clay deposit of probable Cretaceous age is found near Shubenacadie. The material is interstratified with sands, and the whole covered by glacial drift. Some fire-clay has been obtained from it. Similar clay, mottled red and white, outcrops near Middle Musquodoboit and is worked to supply stoneware potteries at St. John, New Brunswick.

Pleistocene

Most of the Pleistocene clays fall into one of two classes, viz.: (1) Glacial clays, often stony, very plastic, tough, and red-burning, and (2) Estuarine clays, usually strongly laminated, plastic and red-burning.

The estuarine clays have been employed for making common brick and drain tile. At Enfield a very smooth clay is used for earthenware pottery.

Analyses of Nova Scotia Clays

	I	II
SiO_2	55.52	74.03
Al_2O_3	26.80	17.30
Fe_2O_3	2.58	1.15
TiO_2	1.50	1.04
MgO	1.05	0.16
CaO	0.25	0.38
Na_2O	0.75	0.53
K_2O	3.43	0 88
H_2O	8.39	4.78
	100.47	100.25

I. Coal-measures clay, Inverness.
II. Fire-clay Shubenacadie.

M. F.Connor, anal. From Can. Geol. Surv., Mem. 16.

REFERENCES ON NOVA SCOTIA CLAYS

1. Faribault, E. R., Clays in Lunenburg County, Nova Scotia, Can. Geol. Surv., Sum. Rept., 1912, p. 383, 1914.
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ONTARIO

Clay-bearing formations.—Those known are the Ordovician, Silurian, Devonian, Mesozoic, and Pleistocene. The deposits are all sedimentary, residual clays being rare.

These formations contain an abundance of clay suitable for the ordinary structural clay products but no high-grade clays are known in the province except the unworked Mesozoic ones of northern Ontario, which cannot be developed until they are more accessible. The surface clays of southeastern Ontario are nearly all of Pleistocene age. They are underlain in eastern and central Ontario by Paleozoic and Pre-Cambrian rocks, and in southern Ontario by Paleozoic ones. The chief exception is a limited area of clay near Hamilton which is residual from the Queenstown shale.

RESIDUAL CLAYS

These are naturally rare on account of the glaciated character of the country, and when found are usually only in small pockets.

One unique deposit is that found in the Helen Mine at Michipicoten, Algoma West. This represents a kaolinized diabase dike which is nearly pure white. It is very plastic, fires light gray, and becomes hard and dense at cone 9 with an absorption of 3 per cent, and a total shrinkage of 20 per cent. It is not fused at cone 20.

ORDOVICIAN

Lorraine formation.—This formation overlies the Utica shale and is more widespread and nearer to the surface than the latter. It contains numerous hard sandy layers and a few thin limestone beds which must be eliminated. Extensive outcrops occur near Toronto and are worked at several localities. It is also used in the Ottawa district but is not worked. Additional outcrops are known on Manitoulin Island and along the shore of Georgian Bay.

The shale is worked by the stiff-mud process, and occasionally dry press. The principal wares made from it are common wire-cut brick, rough-face brick, hollow building-blocks, fireproofing and drain-tile. It burns a light red at a comparatively low temperature, and has a short vitrification range.

Queenston shale.—The Interlake peninsula has a red shale long known as Medina, but lately called Queenston, the name Medina being reserved for an overlying gray sandstone formation. The Queenston shale rests directly on the Lorraine and outcrops more frequently because it occupies the base of the Niagara escarpment for a long distance between Lake Ontario and Lake Huron, whereas the Lorraine shale forms part of the escarpment only near the shore of Georgian Bay.

The Queenston is more homogeneous than the Lorraine and more plastic, mostly reddish brown, partly greenish gray and sandy. It is the most abundant and widely used shale in Ontario, and is partly red and partly buff-burning. It is used for dry-pressed and stiff-mud building-brick, hollow building-blocks, and drain-tile, but has a short firing range.

SILURIAN

The Cabot Head shale and the Salina formation are the only shale-bearing formations of the Silurian. Neither of these is well situated for working and the shales of the Salina do not appear to be suitable for the manufacture of clay products.

DEVONIAN

This contains two shale-bearing formations, the Hamilton and the Huron. The first-named was formerly used for making brick and drain-tile at Thedford.

MESOZOIC

Fire-clays of Mesozoic age, as determined by plant remains, are found beneath glacial deposits in the lowland region around the southern and western portions of Hudson Bay. On the Missinabi River they show as smooth plastic clays of various colors, with seams of lignite. The white clay does not deform at cone 28. On the Mattagami River there are beds of refractory plastic clays, some of white-burning character while others are ferruginous. One bed of black clay has the properties of ball-clay.

These deposits are at present too far from transportation routes or markets to be used, and moreover, there is some doubt regarding their extent.

PLEISTOCENE

Keele (Can. Geol. Surv., Rept. 2045, p. 43) does not attempt the detailed classification of the Pleistocene clays adopted by Baker (Ref. 1) but says: " Owing to the difficulty of applying local names to widely separated and varying deposits the clays in this report will be described according to their economic value." The clays are of two main types, red-burning and cream or buff-burning. Both include clays that are very plastic, stiff in working, and sticky, as well as others which are of low plasticity and easily worked. None of them can be used for vitrified products.

The workable clays of Pleistocene age are mainly of the post-glacial lake and estuarine type. Those of eastern Ontario are mostly of marine origin, while the others were deposited in fresh water. Their properties are sometimes improved by weathering. These clays are extensively worked in many parts of the province for the manufacture of soft-mud and stiff-mud bricks, as well as for structural and drain-tile.

REFERENCES ON ONTARIO CLAYS

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2. Keele, J., Clay and Shale Deposits of the Abitibi and Mattagami Rivers, Ont. Bur. Mines, Rept. XXIX, Pt. 2, p. 31, 1920.
3. Keele, J., Mesozoic Clays and Sands in Northern Ontario, Trans. Roy. Soc. Can., Sec. IV, p. 25, 1921.
4. Keele, J., Preliminary Report on the Clay and Shale Deposits of Ontario, Can. Geol. Surv., Mem. 142, 1924.

ANALYSES OF ONTARIO CLAYS

	I	II	III	IV	V	VI
SiO_2	63.60	43.38	65.04	38.94	69.12	63.00
Al_2O_3	16.49	10.96	16.14	12.10	14.03	15.15
Fe_2O_3	5.27	4.56	6.37	4.83	4.81	6.28
CaO	0.99	18.00	0.80	17.58	1.94	3.48
MgO	2.40	3.33	2.17	4.17	1.10	2.67
Na_2O	1.04	1.30	0.64	0.90	1.53	2.64
K_2O	1.30	2.12	3.21	2.38	2.05	3.11
SO_3	....	....	0.12	0.52	0.10	0.30
Ignition	8.71	16.52	5.98	18.62	4.80	3.63
	99.80	100.17	100.47	100.24	99.48	100.26

I. Hudson River shale, Toronto Junction. Used for paving brick.
II. Hudson River shale, Toronto. Buff burning.
III. Queenston shale, Waterdown.
IV. Erie blue clay, Norwich.
V. Red top clay, Stratford.
VI. Saugeen clay, Bracebridge.

All from Ont. Bur. Mines, XV, 1906.

PHYSICAL TESTS OF ONTARIO CLAYS

		I	II	III	IV	V
		Per cent	Per cent	Per cent	Per cent	Per cent
Water plasticity		24	17	18	28	25
Linear air shrinkage		5	4	4	7	7
Cone 010	Linear fire shrinkage	4	0	*	1	0
	Absorption	6	10	15	22	15
Cone 06	Linear fire shrinkage	6	0	*	1	3
	Absorption	2	8	....	24	13
Cone 03	Linear fire shrinkage	8	0	*	2	6
	Absorption	0	6	15	20	0

* Slight swelling.

I. Lorraine shale, Medford Brick Co., Medford, Grey County.
II. Queenston shale, Milton Pressed Brick Co , Red-burning.
III. Queenston shale, Milton Pressed Brick Co., Buff-burning.
IV. Quaternary clay, London, Middlesex County. Upper calcareous clay, buff-burning.
V. Quaternary clay, Hamilton. Upper clay, red-burning.

All from Can. Geol. Surv., Mem. 142.

PRINCE EDWARD ISLAND

The clay resources of this province are limited to boulder-clays and post-glacial clays.

These post-glacial clays have been used at a number of localities for making of brick and tile. They are red and possess very good working qualities but have a short heat range and soften at a comparatively low temperature.

QUEBEC

Clay- and shale-bearing formations.—The large area of pre-Cambrian rocks which underlies the greater part of the province contains workable deposits of clay at only one locality (Huberdeau), so far as known.

The Silurian and Ordovician formations carry the best shale deposits, but some occur in the Devonian.

Pleistocene clays are widely distributed, and are the ones most used.

Residual Clays

Near Huberdeau, in Amherst township there occurs a deposit of kaolin in Grenville quartzite which is associated with a zone of fracture and faulting traversing both the quartzite and garnet gneiss. The kaolinized zone is about 1000 by 7000 feet, and a shaft 100 feet deep has been sunk.

Wilson (Ref. 2) believes that the kaolin has been formed by rising solutions which attacked the quartz grains and replaced them by kaolinite. At places remains of the vertical beds of quartzite are found in the kaolin. Some of the kaolin is white to cream but other portions are discolored by iron oxide, and also graphite. A heavy mantle of glacial drift covers the deposit. The clay is washed, and the purified product is fairly plastic, has low tensile strength and does not deform at Cone 33. It has been used chiefly as a paper filler, but could also be employed in whiteware bodies. The chemical analysis gave: SiO_2, 46.13; Al_2O_3, 39.45; Fe_2O_3, .72; CaO, 0.00; MgO, 0.00; K_2O, 0.20; Na_2O, 0.09; Ignition, 13.81. Physical tests are given on p. 599, No. VI.

Ordovician

Sillery formation.—This is confined mostly to that portion of the province lying south of the St. Lawrence River between Sherbrooke and Rivière-du-Loup. A small area occurs on the north side of the river south of Quebec City. Much of the formation is so hardened that it does not develop plasticity. The shales are red and gray. Tests of a soft-red shale from St. Charles-de-Bellechase indicate that the material has low plasticity and shrinkage, but is a good vitrifying shale which could be used for dry-press brick, sewer-pipe or paving-brick, but for the two last-named uses it would be necessary to add some of the plastic surface clay to make the material sufficiently plastic. The formation is not used at present.

Levis formation.—Rocks of this formation occupy a small area in the vicinity of Levis. The shales tested are more nearly slates (Ref. 1). When ground they have low plasticity, and so could be used only for dry-press brick, but since they are of vitrifiable character, they might be employed for sewer-pipe or paving-brick if a little plastic clay were added to them.

Utica-Lorraine formations.—These formations contain the most wide-spread shale deposits found in the province. They form a strip of varying width on both sides of the St. Lawrence River between the city of Quebec and Montreal, but occur only in the valley, and not in the bordering uplands. A narrow band is also found on the south shore of the Gulf of St. Lawrence, and there is a small outlier in the Lake St. John basin among the pre-Cambrian rocks.

The shales of the two formations are similar, and hardly distinguishable except by their contained fossils. In character they are grayish to nearly black, often gritty, with little plasticity when ground, and containing a high percentage of fluxing impurities which not only causes low fusibility, but also a short vitrification range.

In the vicinity of Quebec and Levis the shale contains sufficient carbonate of lime to cause a buff color at 1090° C. The Lorraine shales are more gritty than the Utica and often grade into sandstone, while the Utica shales although more uniform, sometimes contain beds of limestone.

The fusibility of these shales limits their use to building-brick and fireproofing, and it is frequently necessary to add some plastic surface clay to improve their working qualities. Some of the Utica shale also contains enough carbon to cause trouble in firing.

Large quantities of common and face brick are made from the Utica-Lorraine shales at La Prairie and Delson Junction in La Prairie County, and at Boischatel, Montmorency County.

SILURIAN

The only shale formations of Silurian age likely to contain workable deposits are those found in the Medina, which occurs in a few small areas in Nicolet County. The lower part of the Medina consists of alternating thin layers of sandstone and sandy shale, but in the upper part there are some thick beds of fairly plastic material containing little sandstone.

This shale is dark-red to reddish-brown, friable, and rather easily eroded. It is easily ground, moderately plastic, dries rapidly without checking and fires to a dense body of good color at a low temperature (cone 010). It cannot be vitrified but appears to be well suited to the manufacture of stiff-mud or dry-press building-brick.

Farther east there are larger areas of Silurian rocks, but the shales are too much metamorphosed to be useful for clay products.

DEVONIAN

Devonian rocks occur in Quebec only on the Gaspé peninsula. They contain beds of gray shale which might be of commercial importance if they were not located so far from the market.

PLEISTOCENE

The greater portion of the surface clays of southern Quebec (except the boulder clays) were apparently deposited in a sea-basin formed by a depression of the land to a depth of about 625 feet. This resulted in a flooding of all the lowlands of the St. Lawrence valley, as a result of which clay covers a large part of this area. In some places the clay is covered by sand, while in others there is sand but no clay. In addition clay is also found underlying terraces up to an elevation of 630 feet.

A large area of Pleistocene clay occurs around Lake St. John at about 500 feet elevation, and in northern Quebec north of the divide between the St. Lawrence and Hudson Bay drainage there is another extensive deposit.

Most of the Pleistocene clays are laminated and often contain sand layers. Those deposits which contain a moderate percentage of silt or sand are better than the highly plastic ones which are hard to work and dry, as well as having a very high shrinkage.

The upper oxidized brown clay also has better working and drying qualities than the lower blue clay.

The low level clays are in general more plastic and sticky, than those found above the 200 feet level, although there are exceptions.

All of the Pleistocene clays are red-burning, and are fired at cones 010 to 07. They are used for common brick and drain-tile, but have too short a firing range to be employed for vitrified products, and are not suited to the manufacture of dry-pressed brick.

At St. Johns the Pleistocene clay is successfully used in a mixture with New Jersey fire-clay for making sewer-pipe. Several plants are making common red brick from the clay along the St. Lawrence River at Deschaillons, because it shows better drying qualities.

Physical Tests of Quebec Clays

		I	II	III	IV	V	VI*
		Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
Water plasticity		16	17	30	35	22	45
Linear air shrinkage		3	3	8.5	9	4.5	7.0
Cone 010	Fire shrinkage	....	0	1.3	0.7	0	3.0
	Absorption	19	11.4	15.7	18	16	34.3
Cone 06	Fire shrinkage	....	0	2.2	4.0	0.5	3.6
	Absorption	17	8.5	15.5	16.6	13.2	34.3
Cone 03	Fire shrinkage	0.6	2	10	10.7	5.3	
	Absorption	....	5.7	0	0	0	
Cone 1	Fire shrinkage	4.6	2	....	....	....	4.5
	Absorption	3	1	....	....	....	32
Cone of fusion		4	3	1	1	2	34

* Cone 5, 9.3 fire shrinkage, 20.0 absorption; Cone 9, 11.3 fire shrinkage, 17.0 absorption.

I. Utica-Lorraine shale, Montmorency.
II. Medina shale, Ste. Monique;
III. Pleistocene brick clay, Lakeside.
IV. Pleistocene brick clay, Montreal.
V. Pleistocene brick clay, St. Raymond.
VI. Washed kaolin, Huberdeau.

REFERENCES ON QUEBEC CLAYS

1. Keele, J., Preliminary Report on the Clay and Shale Deposits of the Province of Quebec, Can, Geol. Surv., Mem. 64, 1915.
2. Wilson, M. E., Geology and Mineral Deposits of a Part of Amherst Township, Quebec, Can. Geol. Surv., Mem. 113, 1919.

SASKATCHEWAN

Clay-bearing formations.—These include the Cretaceous, Tertiary, and Pleistocene. The clay resources of only the southern part of the province have been investigated in fair detail. The Cretaceous and Tertiary beds are practically flat lying.

Cretaceous

Niobrara and Pierre formations.—Both of these formations which underlie much of the central and eastern part of the province, probably contain a large amount of shale, but on account of the covering of Pleistocene deposits outcrops are scarce.

Tests of the Niobrara shale from Lost Mountain Lake north of Regina indicate that it could not be easily used as it is too tough and sticky when mixed with water, will not stand rapid drying, and tends to bloat and black core in the kiln.

The Pierre shale where tested was found to have excessive shrinkage in drying and burning, and to develop a dirty scum in the kiln. It is also frequently gypsiferous.

TERTIARY

The section of the Tertiary in southern Saskatchewan is given as follows:

Oligocene = Cypress Hills formation

$$\text{Eocene (Ft. Union)} = \begin{cases}\text{Ravenscrag}\\ \text{White mud}\\ \text{Estevan}\end{cases}$$

Estevan group.—This contains clays of doubtful value, as they are stiff, sticky, and show excessive shrinkage. One of the beds is being worked and specially treated at Estevan, for making dry-press face brick.

White-mud formation.—The clays of this formation are relatively pure and refractory, in striking contrast to those which lie above and below it.

The eastern beds, as those of the Souris Valley near Halbrite and Yellow Grass, in the Dirt Hills at Claybank and Mitchellton, and in the Lake-of-the-Rivers valley near Willows, are more refractory than those in the Cypress Hills district. Some of the eastern clays are true fireclays while those farther west are semi-refractory clays and stoneware clays.

The only plant in the province using the refractory clays is located at Claybank on the north slope of the Dirt Hills, some 30 miles south of Moosejaw. The clays have a lenticular structure and some of them are very sandy. They are being used for fire-brick and high-grade face brick. No large deposits seem to have been proven.

Clay is mined at Willows and shipped to Medicine Hat to be used in sewer-pipe. The section is as follows:

	Feet
Boulder clay	2
Sticky dark clay with selenite	4
Lignitic clay	1
Purplish-gray clay	15
Lignitic clay	½
Dark gray clay	3
Light gray sandy clay	4
Purplish-gray clay	5
Gray clayey sand	3
Carbonaceous sandy clay	2

The run of bank is not quite vitrified at cone 10. By mixing with it some of the stoneware clay from Eastend a better sewer-pipe has resulted and it can be burned at cone 7.

The 15-foot bed near the top is important. It is a strong plastic clay with 8.3 per cent air-shrinkage, which fires white at cone 03 with a total shrinkage of 12.6 per cent and absorption of 16 per cent. It is not vitrified at cone 9, and deforms at cone 30. Some of the beds in the Willows district yield a good ball-clay (Ref.).

At Eastend there are excellent exposures of the white plastic sewer-pipe clays of the White-mud formation. Stoneware clays could be obtained by selecting certain beds of the series, but it would be necessary to leach out the soluble salts before using. Clays are shipped from here to Medicine Hat for use in stoneware and sewer-pipe manufacture.

PLEISTOCENE

The Pleistocene deposits include glacial lake clays and flood-plain or terrace deposits. Only the more silty clays can be used as the highly plastic ones (gumbo) free from silt are almost impossible to work and crack badly in drying.

PHYSICAL TESTS OF SASKATCHEWAN CLAYS

		I	II	III	IV	V
Water plasticity, per cent		21	27	....	30.0	27.0
Linear air shrinkage, per cent		5	6.1	7.8	8.5	6.1
Tensile strength, pounds per square inch		334	123	....	334	....
Cone 010	Linear fire shrinkage, per cent	*	0.0	1.0	0.2	0.0
	Absorption, per cent	24.48	18.58	14.76	16.38	18.58
Cone 03	Linear fire shrinkage, per cent	*	2.7	3.6	4.4	2.7
	Absorption, per cent	23.94	15.41	11.60	7.52	15.41
Cone 1	Linear fire shrinkage, per cent	0.4	....	6.0	5.4	....
	Absorption, per cent	19.74	....	8.23	4.28	....
Cone 3	Linear fire shrinkage, per cent	....	....	....	5.3	....
	Absorption, per cent	....	....	....	4.39	....
Cone 5	Linear fire shrinkage, per cent	....	2.7	6.6	....	2.7
	Absorption, per cent	....	10.3	4.37	....	10.7
Cone 9	Linear fire shrinkage, per cent	....	3.3	8.4	....	3.3
	Absorption, per cent	....	9.8	2.25	....	9.81
Cone of fusion		2	32	32	....	32

* Slightly swelled.

I. Surface clay, Estevan.
II. Light-gray sandy clay; Dirt Hills.
III. Gray fire-clay, Dirt Hills.
IV. Claybank. Large pieces crack badly on drying. Burns red.
V. Clay bank. Stands rapid drying. Contains soluble salts. Burns white.

Common brick are made at Saskatoon from a surface clay which is a mixture of silty or sandy yellowish clay with a dark gray, stiff, highly plastic clay. The latter will not break down readily but remains as lumps in the brick. The clay is pale red-burning and cannot be vitrified.

Sandy and silty surface clays are also used for common brick at Prince Albert and at Bruno.

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